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Application of Biomass Derived Materials in Nanocomposites and Drilling Fluids

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APPLICATION OF BIOMASS DERIVED MATERIALS IN
NANOCOMPOSITES AND DRILLING FLUIDS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The School of Renewable Natural Resources

by
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ABSTRACT

Tar is inevitably produced from biomass thermochemical processes, and is often disposed as an industrial waste, leading to environmental pollution. As a result of its high carbon content, tar was expected to be a promising precursor for manufacturing carbon materials. Consequently, low-cost porous carbon nanofibers (CNFs) using tar, polyacrylonitrile (PAN), and silver nanoparticles was fabricated through electrospinning and subsequent stabilization and carbonization processes. The continuous electrospun nanofibers were obtained with diameters ranging from 392 to 903 nm. The addition of biomass tar resulted in increased fiber diameters, reduced thermal stabilities, and slowed cyclization reactions of PAN in the as-spun nanofibers. After stabilization and carbonization, the produced CNFs showed more uniformly sized and reduced average diameters. The CNFs exhibited high specific surface areas (>400 m²/g) and microporosity. These porous features increased the exposures and contacts of silver nanoparticles to the bacteria, leading to excellent antimicrobial performances of as-spun nanofibers and CNFs. A new strategy is thus provided for utilizing tar as low-cost precursor to prepare functional CNFs and reduce environmental damage by direct disposal of tar.

Additionally, nanocellulose, was used as an environmental friendly and high performance additive in drilling fluids for improving rheological and fluid filtration properties. Two types of nanocellulose, including cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), were applied in the drilling fluids. The effects of nanocellulose dimensions and concentrations on the rheological and filtration properties of drilling fluids were investigated. With half of the bentonite (10 lb/bbl) replaced by a small fraction of nanocellulose (0.35-3.50 lb/bbl), the resultant low-solid drilling fluids showed excellent shear thinning behavior and the fluids’ viscosity, yield point, and gel strength increased with the concentrations of nanocellulose. On the
other hand, the addition of nanocellulose reduced the fluid loss of the fluids under high temperature and high pressure (HTHP) conditions, demonstrating potential for HTHP well applications. Additionally, the CNCs and CNFs behaved differently in the rheological and fluid filtration properties attributed to their distinct morphologies. This study promoted the use of novel renewable biopolymer additives in drilling fluids with enhanced performance and advantages of low cost and ecologically friendly.
CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

Energy shortage, environmental pollution, and global warming have been becoming crucial issues that drive us to utilize renewable natural resources with less environmental harm in a sustainable way. Biomass is one of the promising alternatives to petroleum-based energy and materials with attractive characteristics including abundance, renewability, and carbon neutrality. However, biomass has not been fully utilized and emerged issues accompanying its applications have not been efficiently addressed. On one hand, biomass can be converted to products for substituting petrochemical-derived energy and materials through pyrolysis or gasification. During these processes, tar is inevitably produced and often disposed as an industrial waste, causing environmental pollution. Meanwhile, tar contains many valuable components that may be utilized for manufacturing of chemicals and carbonaceous materials. Accordingly, an efficient way to manufacture tar derived composite materials is required urgently. On the other hand, biomass is composed of cellulose, hemicellulose, lignin, small amounts of lipids, proteins, and inorganic constituents as well as a fraction of water. Nanocellulose isolated from biomass is widely used for reinforcing polymeric composites as a result of its high strength and nanodimensions. In addition, cellulose is a thermally stable, biodegradable, nontoxic, and readily available biopolymer that can be used as a lost circulation, rheological, and filtration control material in oil and gas well applications.

1.1.1 Biomass Tar in Carbon Materials

Through thermochemical transformation, including gasification and pyrolysis, biomass generates gases, liquids and solid fuels which can partially be the substitutes for fossil fuels (Milne et al., 1998). However, tar is an inevitable by-product during these processes and the
most cumbersome and problematic parameter in any biomass gasification commercialization activities. A lot of effort has been taken on physical removal and chemical conversion of the tar from biomass conversion (Milne et al., 1998). However, these processes need a lot of energy input and may induce other problems such as the treatment of the more refractory secondary products from physical removal and chemical conversion of tar. Therefore, further fundamental knowledge about the chemical composition and properties of tar is needed to better control its conversion and separation during biomass conversion. Meanwhile, it is crucial to find good ways of utilizing biomass tar and turn the unavoidable “waste” into wealth, which can serve as the alternative method to control the accumulation of tar and reduces dramatically its harm to environment.

Chemical composition of biomass tar is highly complex and dependent on the feedstock of biomass and thermochemical conversion conditions such as oxygen level, steam-to-biomass ratio, pressure, time, and temperature (Aigner et al., 2009; Ku and Mun, 2006; Yanik et al., 2007). Biomass tar is defined as a complex mixture of condensable hydrocarbons, including single ring to five-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbon (PAH) (Li and Suzuki, 2009b). However, no further details about the composition and structure of tar components were investigated. As a result, it is desirable to obtain a comprehensive knowledge of the chemical composition of biomass tar at a higher level of detail. Besides the chemical composition of tar, its thermal decomposition properties also play a crucial role in its successful control, conversion and further application. Biomass tar decomposition mainly occurs due to cracking, steam reforming, dry reforming and carbon formation reactions (Li and Suzuki, 2009a). It is difficult to study the thermal degradation of tar because of its complex composition. Most of previous researches simplify the tar
decomposition analysis by selecting a model compound of tar such as naphthalene (Anis et al., 2013; Devi et al., 2005), toluene (Kong et al., 2011; Swierczynski et al., 2008), benzene (Simell et al., 1999) and 1-methylnaphthalene (Dou et al., 2003). However, only one model component can’t reflect the decomposition reaction mechanism of real tar and the interactions of its components. Therefore, the thermal decomposition of biomass tar has not been fully characterized and understood until now and further systemic study on tar is required to reveal its complex thermal degradation mechanism.

Although tar is an undesirable product for biomass gasification and pyrolysis, it can be a valuable carbon precursor of carbonaceous materials, including carbon fibers, porous carbon, and carbon foam, considering its high carbon content (Song et al., 2015). Different carbon materials have been fabricated and characterized using coal or petroleum derived pitch which has a similar composition to tar. Using isotropic pitch, activated carbon fibers have been prepared, which exhibit a high surface area (>2000 m²/g), high electrical conductivity (>50 s/cm), high carbon yield (60 %) at 1000 °C, and high adsorption ability (Bui et al., 2009; Park et al., 2003). A modification of pitch-based carbon fibers using low-cost carbon black was reported to improve the electrical and thermal conductivity, making them more favorable for industrial application (Alway-Cooper et al., 2013). In addition, porous carbon has been prepared using pitch as a carbon precursor. Using soft-templating-based methodology, meso- and macroporous carbon have been synthesized, taking advantage of the phase separation (spinodal decomposition) of mesophase pitch, which acts as the carbon precursor, and an organic polymer (polystyrene), which acts as the template (Adelhelm et al., 2007). The main idea behind this approach is to induce continuously increasing incompatibility between mesophase pitch and the polymer during the evaporation of the solvent and the subsequent carbonization step. Besides carbon fibers and
porous carbon, pitch can be used to produce carbon foam materials (Chen et al., 2006). This material is a sponge-like carbon material with the features of low density (0.2-0.8 g/cm$^3$), good thermal stability, high mechanical strength (up to 20 MPa, compression), large external surface area with open cell structure, and adjustable thermal and electrical conductivity, which has potential applications in high temperature thermal insulation materials, high thermally conductive heat sinks, electrodes for energy storage, catalyst supports and filters (Chen et al., 2006; Wu et al., 2011). However, carbon materials produced by tar from biomass conversions have not been reported. Consequently, it is expected to manufacture biomass tar-based carbon materials using this abundant and low-cost carbon precursor.

1.1.2 Cellulose Nanoparticles in Drilling Fluids

Drilling fluids, commonly referred to as drilling muds, are an integral part of drilling oil and natural gas wells. A drilling fluid is typically pumped through the drill string and is subsequently introduced to the bottom of the bore hole as it squirts out of nozzles on the drill bit. The drilling fluids have various functions, including controlling formation pressures, minimizing formation damage, maintaining wellbore stability, suspending and carrying out cuttings, and cooling and lubricating drilling bit (Bourgoyne et al., 1991). The successful drilling operations are highly dependent on the selection of drilling fluids with desirable performance.

Facing increasing drilling challenges in complex deeper wells, deviated wells, and horizontal wells, the oil and gas industry is always looking for physically small, chemically and thermally stable, biologically degradable, environmentally benign materials for designing smart drilling fluids with desirable performance (Abdo and Haneef, 2013). Recently, the nano-based drilling fluids loaded with nanoparticles are attracting more attention due to their unique characteristics such as a high surface area to volume ratio. Such nanoparticles play an essential
role in decreasing the permeability of shale formation, maintaining borehole stability, intensifying mud cake quality, reducing fluid loss, improving cutting removal ability, lowering the friction, eliminating differential pipe sticking, protecting reservoir, and enhancing oil and gas recovery (Abdo and Haneef, 2013; Farbod et al., 2015; Sun et al., 2015). Due to these advantages, addition of nanoparticles into drilling fluids can improve drilling efficiency, save drilling cost, and protect the environment.

A variety of nanoparticles have been studied for preparing nano-based drilling fluids, including nano-silica (Sensoy et al., 2009; Sharma et al., 2012), nano metallic oxide (Cheraghian et al., 2013; Sayyadnejad et al., 2008), carbon black, nano-graphite (Nasser et al., 2013), polymer-based nanoparticles (Jiang et al., 2009; Qu et al., 2007), and combinations of these. However, the use of these nanoparticles is limited by their cost and environmental impact. Furthermore, with an increasing pressure from energy shortages and ecological deterioration, renewable natural resources such as cellulose, starch, and protein are intensively studied to substitute for non-renewable petroleum-based products.

Cellulose is the most abundant natural resource in nature, which widely exists in various natural fibers, such as wood, cotton, hemp, and linen. Cellulose derivatives such as polyanionic cellulose (PAC) and carboxymethyl cellulose (CMC) have been the popular additives to optimize the rheological properties of drilling fluids (Li et al., 2016; Menezes et al., 2010). However, they have been added as particles with a large size ranging from several micrometers to millimeters. Much smaller particles, named as nanocellulose, can currently obtained through several physical and chemical methods, such as acid hydrolysis, enzyme hydrolysis, 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) mediated oxidation methods, and a high pressure homogenization (Moon et al., 2011). Nanocellulose has high surface to volume ratio, much lower density of 1.6
g/cm$^3$ than silica (2.2 g/cm$^3$), and high values of tensile strength (7.5-7.7 GPa) and axial elastic modulus (110-220 GPa) (Moon et al., 2011). Because of these excellent characteristics, nanocellulose can be used for preparing technically reliable, economically attractive, environmentally friendly drilling fluids to meet the technical needs and challenges of the oil and gas industry.

1.2 OBJECTIVES

The objectives of the research described in this work are:

1) To investigate the chemical composition and thermal degradation of biomass tar obtained from corn stover gasification, aiming at facilitating the further processing and utilization of biomass tar.

2) To fabricate functional nanofibers prepared by electrospinning biomass tar/PAN suspensions. The electrospinnability of the tar/PAN suspensions as well as the structure and properties of the resultant nanofibers with varying tar contents were investigated.

3) To manufacture low-cost porous carbon nanofibers (CNFs) using biomass tar, polyacrylonitrile (PAN), and silver nanoparticles through electrospinning and subsequent stabilization and carbonization processes. The effects of tar loading levels on electrospinning ability of the suspensions, morphologies, chemical structures, thermal properties, pore features, and antimicrobial performance of resultant CNFs were investigated.

4) To develop drilling fluids with low solid content by substituting nanocellulose, including cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs), for a part of bentonite in the fluid system. The effects of cellulose nanoparticle content on the rheology and fluid filtration properties of the resultant drilling fluids were studied.
1.3 ORGANIZATION OF DISSERTATION

Chapter 1 provides an overall introduction of the research and the structure of this dissertation.

Chapter 2 introduces the chemical composition and thermal properties of tar from biomass gasification.

Chapter 3 describes the fabrication and characterization of electrospun nanofibers from PAN and biomass tar.

Chapter 4 presents the fabrication and characterization of porous carbon nanofibers from PAN/biomass tar/silver by electrospinning, thermal oxidation, and carbonization processes.

Chapter 5 describes the preparation of low solid drilling fluids added with nanocellulose and investigates the effects of nanocellulose content on the rheology and fluid loss properties of the drilling fluids.

Chapter 6 presents the formulation of drilling fluids having compositions very similar to the field fluids under use, including bentonite, nanocellulose, and other additives. The rheological and filtration properties of the formulated fluids were tested and special emphasis was put on the performance of the fluids under high temperature and high pressure conditions.

1.4 REFERENCES


CHAPTER 2 STRUCTURE AND THERMAL PROPERTIES OF TAR FROM GASIFICATION OF AGRICULTURAL CROP RESIDUE

2.1 INTRODUCTION

Energy shortage, environmental pollution, and global warming have been becoming crucial issues in the past few decades. Biomass from industrial crops such as straw and corn stover is one of the promising alternatives to petroleum-based resources for meeting society’s increasing demand for material and energy (Ghani et al., 2013). Through thermochemical transformation, including pyrolysis and gasification, biomass generates gases, liquids, and solid fuels. Tar is an inevitable by-product in the thermal conversion processes of biomass. The disposal of tar is very cumbersome and costly. The usual methods such as landfiling can lead to environment contamination due to tar’s high resistance to degradation (Li and Suzuki, 2010). On the other hand, tar is a valuable resource for chemicals and carbonaceous materials. For example, tar has been used for the substitution of phenol in phenol-formaldehyde (PF) resins (Lu and Wu, 2013), wood preservatives (Suzuki et al., 1997), and utilized for the preparation of activated carbon fibers (Bui et al., 2009). Understanding of the chemical structure and thermal properties of tar is essential for enhancing the performance of the resultant materials.

Tar represents a complex mixture of condensable hydrocarbons, including single ring to five-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs) (Li and Suzuki, 2009b). Its chemical composition depends on the sources of biomass and thermochemical conversion conditions (Aigner et al., 2009; Ku and Mun, 2006; Yanik et al., 2007). The structure of pitch from coal or petroleum has

been well investigated (Alcañiz-Monge et al., 2001; Jiang et al., 2007; Sun et al., 2011). However, little attention has been paid to the chemical composition of tar from biomass gasification or pyrolysis. Therefore, it is necessary to quantitatively characterize the constituents of tar to facilitate its further processing and utilization.

Aside from the chemical composition of tar, its thermal degradation behavior also plays an essential role in understanding the thermal stability properties of tar derived chemicals and materials. Decomposition of tar mainly occurs through cracking, steam reforming, dry reforming and carbon formation reactions (Li and Suzuki, 2009b). Previous research has focused on combustion properties of tar from different biomass sources in the presence of oxygen or catalysts (Li and Suzuki, 2009b; Li et al., 2009). However, few studies have considered the thermal behavior of tar under controlled inert atmosphere. In addition, tar decomposition analysis has been frequently simplified by selecting a model compound of tar such as naphthalene (Devi et al., 2005), toluene (Swierczynski et al., 2008), benzene (Simell et al., 1999) and 1-methylnaphthalene (Dou et al., 2003). However, a single model component cannot reflect the complex decomposition reaction mechanism of real tar and the interactions of its components. Thus, thermal analysis performed on the entire tar material is required.

The objective of this study was to investigate the chemical composition and thermal degradation of biomass tar obtained from corn stover gasification, aiming at facilitating the further processing and utilization of this promising biomaterial. The tar composition was characterized by gas chromatography-mass spectroscopy (GC-MS), Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. Thermogravimetry with multiple-heating rates under non-isothermal conditions was used to provide data for thermal kinetic analysis of this material.
2.2 MATERIALS AND METHODS

2.2.1 Materials

Tar was produced by gasification of corn stover feedstock at 500-600 °C in Xigou Biomass Fuel Gas Plant (Xihe, Shanxi, China). The plant used fixed bed downdraft gasifiers, producing about 200 m$^3$ of fuel gas per hour mainly for cooking uses. The gasification efficiency was about 75% and total energy output was about 1.1×10$^9$ J/h. The plant consumed about 180 tons of agricultural residues per year. The collected tar material was vacuum dried to remove the water at 80 °C and then placed in a sealed container for further analysis.

2.2.2 Characterization

2.2.2.1 GC-MS Analysis

The dried tar (5 g) was added into ethyl acetate (50 mL) with a ratio (tar/solvent = 1 g/10 mL). The obtained mixture was kept under vigorous magnetic stirring at room temperature for 24 h. The resulting suspension was centrifuged for 30 min and the upper liquid fraction was collected and diluted to a mass concentration of 0.5 % for GC-MS analysis (Figure 2.1). The solid fraction was dried in vacuum at 80 °C and weighed (1.41 g) prior to elemental analysis. The liquid fraction had a mass of 3.60 g tar in ethyl acetate, taking up 71.80 wt% of the original dried tar. A HP-3800 gas chromatograph (GC) equipped with split/splitless injector and a HP-8410 automatic sampler with splitless injection were used to analyze the composition of tar. The injector was maintained at 250 °C with helium as the carrier gas at a flow rate of approximately 1.0 mL/min. The GC was equipped with a 30 m (length) × 0.25 mm (inner diameter) Hewlett Packard HP-5MS capillary column. The oven temperature was kept at 40 °C for 3 min, and then heated to 200 °C at 15 °C/min, followed with further heating to 280 °C at 1 °C/min. This temperature was held for 5 min. The end of the column was directly introduced into the ion
source of a HP 5970 mass selective detector (MSD) with electron ionization (EI) mode. During the test, the transfer line was set at 270 °C, ion source was kept at 250 °C, and electron energy remained at 70 eV. The data acquisition was done with HP-UX chemstation software associated with a HP-UNIX computer and NBS mass spectra library database. The quantitative evaluation was based on the relative percent areas of the single peaks related to the total peak area.

Figure 2.1 Scheme illustrating the drying and centrifuging processes of biomass tar for GC-MS analysis

2.2.2.2 FTIR Spectroscopy

A Bruker FTIR analyzer (Tensor-27, Bruker Optics Inc., Billerica, MA) equipped with an attenuated total reflectance (ATR) cell of ZnSe single crystal was used for the study. The FTIR spectra of the dried tar and the residue after its decomposition at 600 °C by a heating rate of 10 °C/min in N₂ atmosphere were recorded. Each spectrum was recorded by accumulation of 32 scans in N₂ atmosphere with a spectral resolution of 4 cm⁻¹ between 4000 and 700 cm⁻¹. The baseline was corrected at 3750, 1800, and 700 cm⁻¹ by the attached software (OPUS 7.2, Bruker).

2.2.2.3 Elemental Analysis

The elemental composition of tar was analyzed using a Perkin-Elmer automatic CHN analyzer (Atlantic Microlab, Inc., Norcross GA, USA). The content of C, H, and N was obtained
directly, while the oxygen content was determined by the difference in mass between the initial tar and the total mass of C, H, and O. In this study, the dried whole tar and thermally treated tar with different temperatures (180, 250, 350, and 600 °C for 1 h) and N₂ atmosphere were analyzed and compared.

2.2.2.4 Thermogravimetry (TG) Analysis

A TA Q50 analyzer (TA Instruments Inc., New Castle, DE, United States) with a resolution of 0.1 μg was used to study the thermal decomposition of the tar. Non-isothermal conditions from 30 to 800 °C were applied at various heating rates of 5, 10, 15, 20, 25, and 30 °C/min in the N₂ atmosphere (60 mL/min). The material was ground into powder and dried in vacuum at 80 °C for 48 h prior to analysis. A sample of 5-10 mg was used for each measurement. At least three replicated samples were run at each heating rate to guarantee the repeatability and reliability of data. The mass loss curves (TG) and differential TG curves (DTG) were recorded as a function of temperature.

2.2.2.5 Thermal Kinetic Analysis

The thermal analysis kinetics of solid state reaction is commonly based on a single-step kinetic equation (Brown et al., 1980):

\[ \frac{d\alpha}{dt} = K(T)f(\alpha) \]  \hspace{1cm} (2.1)

where \( K \) is the temperature-dependent reaction rate constant, \( T \) is the temperature, \( f(\alpha) \) is a reaction function depending on actual reaction mechanism, and \( d\alpha/dt \) is the rate of biomass conversion. The extent of conversion, \( \alpha \), is defined as:

\[ \alpha = \frac{(W_0 - W_t)}{(W_0 - W_f)} \]  \hspace{1cm} (2.2)
where $W_0$, $W_t$, and $W_f$ are the mass of the sample during the decomposition process at the initial, given time, and final moment, respectively. The reaction rate constant ($K$), is commonly described by the Arrhenius equation:

$$K(T) = A \exp\left(-\frac{E}{RT}\right)$$ (2.3)

where $A$ is the pre-exponential factor ($s^{-1}$), $R$ is the universal gas constant (8.314 J/(K·mol)), $E$ is the apparent activation energy (kJ/mol), and $T$ is the absolute temperature (K). Combination of Eq. 2.1 and Eq. 2.3 gives the following kinetic function:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)$$ (2.4)

Thermal analysis kinetic study is usually carried out in an isothermal or a non-isothermal experiment. The former process is completed in narrower temperature ranges and truly isothermal conditions cannot be gained for the very low and high reaction extent ($\alpha$) resulting partially from self-heating or self-cooling (Maciejewski, 2000). The non-isothermal method is suitable for a broader temperature range to detect the complex nature of multi-step solid state reaction processes (Maciejewski, 2000). For dynamic non-isothermal analysis, the heating rate is defined as $\beta = \frac{dT}{dt}$. Thus, the basic expression to obtain the kinetic triplet [$E$, $A$, and $f(\alpha)$] based on experimental data can be described as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha)$$ (2.5)

The analytical methods used to obtain the kinetic parameters under non-isothermal conditions generally include model-fitting and model-free methods. The former approach is considered as insufficient in non-isothermal kinetic studies, considering the limited applicability of single heating rate data (Burnham, 2000; Khawam and Flanagan, 2005). On the other hand, the model-free methods based on multi-heating rates and iso-conversional data are more helpful in the kinetic analysis (Vyazovkin et al., 2011). The method has been effective to obtain the
thermal kinetic parameters of biomass (Li and Suzuki, 2009a; López et al., 2013). The Friedman method and the distributed activation energy model (DAEM) are two common model-free methods.

The Friedman method is a differential iso-conversational method, assuming a single \( n \)-th-order reaction occurs, which is based on the below function by taking the natural logarithm of Eq. 2.5:

\[
\ln(\beta \frac{d\alpha}{dT}) = \ln A + \ln[f(\alpha)] - \frac{E}{RT}
\]  

(2.6)

For a particular reaction order model, replacing \( f(\alpha) \) by \((1-\alpha)^n\) gives the following function:

\[
\ln(\beta \frac{d\alpha}{dT}) = \ln A + n\ln(1 - \alpha) - \frac{E}{RT}
\]  

(2.7)

By plotting \( \ln(\beta \frac{d\alpha}{dT}) \) against \(1/T\), the apparent activation energy (\(E\)) and the pre-exponential factor (\(A\)) at a given conversion rate (\(\alpha\)) can be obtained from the slope and intercept of the linear portion of the plot.

The DAEM method was originally proposed by Vand (Vand, 1943) and further developed (Miura and Maki, 1998) to describe complex reactions by assuming that a set of parallel irreversible \(1^{st}\) order reactions occur simultaneously (Miura, 1995; Miura and Maki, 1998). The model has the following form:

\[
1 - \alpha = \int_{0}^{\infty} \exp\left(-k \int_{0}^{E} e^{-E/RT} \, dt\right) f(E) \, dE
\]  

(2.8)

where \(f(E)\) is the distribution of activation energies representing different reactions, and \(k\) is the frequency factor corresponding to the \(E\) value. Through theoretical derivation and approximation [26], a simplified equation is obtained as:

\[
\ln(\beta/T^2) = \ln(kR/E) + 0.6075 - \frac{E}{RT}
\]  

(2.9)

At a selected extent of conversion, \(E\) and \(A\) can be determined by plotting \(\ln(\beta/T^2)\) against \(1/T\). Thus, the relationship between activation energy and extent of conversion can be also
obtained. At least three sets of data are needed in the DAEM method. Six heating rates (5, 10, 15, 20, 25, and 30 °C/min) were selected in this study.

2.3 RESULTS AND DISCUSSION

2.3.1 Chemical Composition

The chemical composition of the tar from the GC-MS analysis is presented in Table 2.1. The tar was composed mainly of phenols and PAHs, representing approximately 80 % of the dissolved tar in ethyl acetate in the molecular mass range from 94 to 202 (Table 2.1). Phenols accounted for 45 % of the tar, including phenol, ethylphenol, methylphenol, dimethylphenol and methoxyphenol. The PAHs mainly consisted of naphthalene, methylnaphthalene, acenaphthylene, anthracene, biphenyl, fluoranthene and phenanthrene, which accounted for 31 % of the soluble tar in ethyl acetate. Besides, the tar contained 7 % of furans and 17 % of other materials, such as aliphatics, esters, acids, etc. Thus, the main components of the tar were phenols and PAHs, similar to the results found in the investigation on tars from wood and bamboo (Ku and Mun, 2006; Mun and Ku, 2010). It was found that at higher temperatures more phenolics and hydrocarbons were formed in biomass tars (Elliott, 1988). The tar in this study was produced from biomass gasification at around 500-600 °C and had 45 % phenols and 31 % PAHs, which was in an agreement with the results from previous studies.

The typical IR detectable functional groups in the tar (Figure 2.2) are listed in Table 2.2. These data were similar to those of other tars reported in the literature (Pakdel and Roy, 1991; Prauchner et al., 2001). The IR spectra showed that the tar contained methylene groups (2923, 2854 cm⁻¹) rather than methyl groups. The aromatic structure was indicated by the IR bands at 3060, 1597, 1512, 830, and 750 cm⁻¹. The absorption at 1265 and 1036 cm⁻¹ were asymmetrical and symmetrical stretching of aryl-alkyl ethers associated with aromatic rings. In addition, the IR
Table 2.1 Chemical components of the biomass tar by GC-MS

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Molecular Weight</th>
<th>Relative Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-ethyl-phenol</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O</td>
<td>122</td>
<td>9.44</td>
</tr>
<tr>
<td>Phenol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O</td>
<td>94</td>
<td>7.49</td>
</tr>
<tr>
<td>3-methyl-phenol</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O</td>
<td>108</td>
<td>6.38</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>128</td>
<td>6.14</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>152</td>
<td>5.69</td>
</tr>
<tr>
<td>2,3-dihydro-Benzofuran</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O</td>
<td>120</td>
<td>5.30</td>
</tr>
<tr>
<td>Anthracene</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>178</td>
<td>4.61</td>
</tr>
<tr>
<td>2-methyl-phenol</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O</td>
<td>108</td>
<td>3.51</td>
</tr>
<tr>
<td>4-ethyl-2-methoxy-phenol</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>152</td>
<td>3.43</td>
</tr>
<tr>
<td>1-methyl-naphthalene</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>142</td>
<td>3.26</td>
</tr>
<tr>
<td>2-methyl-naphthalene</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>142</td>
<td>2.58</td>
</tr>
<tr>
<td>2,5-dimethyl-phenol</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O</td>
<td>122</td>
<td>2.26</td>
</tr>
<tr>
<td>2-methoxy-4-vinylphenol</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>150</td>
<td>2.24</td>
</tr>
<tr>
<td>2,4-dimethyl-phenol</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O</td>
<td>122</td>
<td>2.22</td>
</tr>
<tr>
<td>4-ethyl-3-methyl-phenol</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O</td>
<td>136</td>
<td>2.02</td>
</tr>
<tr>
<td>1H-phenalene</td>
<td>C&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>166</td>
<td>2.02</td>
</tr>
<tr>
<td>Dibenzoferan</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O</td>
<td>168</td>
<td>1.60</td>
</tr>
<tr>
<td>2-methoxy-phenol</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>124</td>
<td>1.59</td>
</tr>
<tr>
<td>2,3-Dimethylhydroquinone</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>138</td>
<td>1.58</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>154</td>
<td>1.56</td>
</tr>
<tr>
<td>2,6-dimethoxy-phenol</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>154</td>
<td>1.55</td>
</tr>
<tr>
<td>1,7-dimethyl-naphthalene</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
<td>156</td>
<td>1.53</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>202</td>
<td>1.45</td>
</tr>
<tr>
<td>2,6-dimethoxy-4-(2-propenyl)-phenol</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>194</td>
<td>1.43</td>
</tr>
<tr>
<td>1,1'-(1,3-butadiyne-1,4-diyl)bis-benzene</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>202</td>
<td>1.22</td>
</tr>
<tr>
<td>2-ethenyl-naphthalene</td>
<td>C&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>154</td>
<td>1.20</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>178</td>
<td>1.11</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td>15.59</td>
</tr>
</tbody>
</table>
stretching of carbonyl groups at 1686 cm\(^{-1}\) was lower than the typical stretching of carbonyl at 1715 cm\(^{-1}\) in ketone, which was probably caused by the conjugation of carbonyl groups with aromatic structure and the delocalization of π electrons (Silverstein et al., 2005). In summary, the FTIR spectra indicated the predominance of phenols, aromatic structures, ethers, aliphatic, and carbonyl groups, which agreed well with the GC-MS data. These groups disappeared in the residue after thermal degradation, indicating that the main components of the biomass tar decomposed completely at 600 °C in the N\(_2\) atmosphere (Figure 2.2).

![Figure 2.2 FTIR spectra of the original tar and the tar after thermal treatment at 600 °C under N\(_2\) atmosphere](image)

The elemental analysis showed the enrichment of carbon from ca. 50 % (in biomass) to ca. 75 % in the tar, but the oxygen content of the tar at ca. 15 % was still high. Temperature treatment up to 600 °C decreased the oxygen content from ca. 16 to 13 % (Table 2.3). The high oxygen content in comparison with fossil pitches (Alcañiz-Monge et al., 2001) was a problem from the energetic point of view. On the other hand, biomass tar was more reactive as indicated by the higher H/C and O/C values compared to fossil pitches (Alcañiz-Monge et al., 2001), which was supported by its constituents (aliphatics, esters, acids, carbonyl, etc.) based on GC-
MS and FTIR analysis. The values of H/C and O/C largely decreased when the thermal treatment temperature reached 600 °C. It was proposed that thermal-chemical conversion of tar was associated with volatilization of low molecular mass hydrocarbons and reactions such as dehydrogenation, condensation and polymerization through the loss of side alkyl groups from aromatic compounds (Lewis, 1987). Therefore, the decreased H/C and O/C values at higher thermal treatment temperatures were probably caused by dehydrogenation and the loss of side groups such as aliphatic groups associated with aromatic rings.

Table 2.2 The IR absorption bands for functional groups of the biomass tar

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional Groups</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>3271</td>
<td>O-H Stretching</td>
<td>Phenols</td>
</tr>
<tr>
<td>3060</td>
<td>C-H Stretching</td>
<td>Aromatic</td>
</tr>
<tr>
<td>2923, 2854</td>
<td>CH₂ Asymmetrical and symmetrical stretching</td>
<td>Alkyl, aliphatic</td>
</tr>
<tr>
<td>1686</td>
<td>C=O stretching</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>1597</td>
<td>Aromatic skeletal vibration together with C=O stretching vibration</td>
<td>Aromatic</td>
</tr>
<tr>
<td>1512</td>
<td>Aromatic skeletal vibration</td>
<td>Aromatic</td>
</tr>
<tr>
<td>1450</td>
<td>CH₂ Symmetrical bending vibration</td>
<td>Alkyl, aliphatic</td>
</tr>
<tr>
<td>1265, 1036</td>
<td>C-O-C Asymmetrical and symmetrical stretching</td>
<td>Aryl-alkyl ether</td>
</tr>
<tr>
<td>1115</td>
<td>C-O-C Asymmetrical stretching</td>
<td>Dialkyl ethers</td>
</tr>
<tr>
<td>830, 750</td>
<td>C-H out-of-plane bending</td>
<td>Aromatic</td>
</tr>
</tbody>
</table>

Table 2.3 Elemental analysis of biomass tar

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>H/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>75.13</td>
<td>6.67</td>
<td>2.56</td>
<td>15.64</td>
<td>0.089</td>
<td>0.208</td>
</tr>
<tr>
<td>180 °C</td>
<td>76.05</td>
<td>6.22</td>
<td>2.55</td>
<td>15.18</td>
<td>0.082</td>
<td>0.200</td>
</tr>
<tr>
<td>250 °C</td>
<td>76.72</td>
<td>5.95</td>
<td>2.85</td>
<td>14.48</td>
<td>0.078</td>
<td>0.189</td>
</tr>
<tr>
<td>350 °C</td>
<td>79.11</td>
<td>5.15</td>
<td>3.37</td>
<td>12.37</td>
<td>0.065</td>
<td>0.156</td>
</tr>
<tr>
<td>600 °C</td>
<td>80.83</td>
<td>2.83</td>
<td>3.27</td>
<td>13.07</td>
<td>0.035</td>
<td>0.162</td>
</tr>
</tbody>
</table>

a The tar after being dried by vacuum;
b The tar by thermal treatment at 180 °C under nitrogen atmosphere;
c The ratio of hydrogen and carbon determined by mass.
2.3.1 Thermal Decomposition

Figure 2.3 Thermal gravimetric curves of biomass tar at different heating rates under nitrogen atmosphere (a); the temperature dependence of the extent of conversion (α) for different heating rates (b)

Typical TG profiles of the tar at different heating rates are presented in Figure 2.3a. The onset decomposition temperature (defined as the temperature at the mass loss of 5 %) was within the range of 133-162 °C, depending on the heating rates. The DTG curves showed one distinct peak between 183 °C (5 °C/min) and 252 °C (30 °C/min) under each heating rate, indicating the highest decomposition rate of the tar. Under all heating conditions, the final solid residue was in the range of 28-30 % at 600 °C. The onset and main thermal degradation temperatures of the tar were slightly lower, compared with previously studied biomass feedstock, such as wood (Shen et al., 2011), corn stover (Ma et al., 2013), and other agricultural residue (Yao et al., 2008; Yi et al., 2013). This could be attributed to relatively low molecular mass components in the tar formed by the breakdown of high molecular mass lignocellulosic materials during biomass gasification. The thermal decomposition process of the tar occurred in a wide temperature range at each heating rate, indicating the complex chemical composition of the tar (confirmed by the GC-MS and FTIR analysis). The peak of mass loss rate in the DTG curves shifted toward higher temperatures with the increasing heating rates (Figure 2.3b). This was due to the heat transfer lag at higher heating rates. However, the final mass loss of tar was not affected by the heating rates.
The kinetic parameters from the Friedman and DAEM models are determined by the isoconversional method, and the data is presented in Figure 2.4 with the extent of conversion ($\alpha$) plotted as a function of temperature. The Friedman method simplified the decomposition of tar as a single reaction and the extent of conversion behaved as a global degradation rate, to which all tar components contributed as a uniform group. The DAEM method assumed a set of parallel irreversible 1st order reactions occurring simultaneously. This approach was widely applied for the thermal kinetic analysis of biomass, including agricultural residues (Ma et al., 2013; Sonobe and Worasuwannarak, 2008), wood (Shen et al., 2011) and pyrolysis products from fowl dropping (Li and Suzuki, 2009b). The Arrhenius plots of $\ln(\beta d\alpha/dT)$ as a function of $1/T$ by Friedman method and $\ln(\beta/T^2)$ against $1/T$ by the DAEM method are shown in Figure 2.4. Linear and parallel relationships were observed from the conversion range of 0.1-0.6, indicating unchanged activation energies at this stage. Accordingly, the thermal decomposition of the tar could be described as a set of parallel single reactions or a uniform multiple reaction mechanism within the conversion rates of 0.1-0.6. The unsatisfactory parallelity of the plots at higher conversion rates ($\alpha>0.6$) indicated the change of reaction mechanism, which was interpreted as a sign of a multiple-step reaction mechanism (Ozawa, 1965). The change of reaction mechanism at
higher conversion rates could be due to the complex reactions in the thermal decomposition process of the main components in the tar (Yao et al., 2008).

Figure 2.5 The activation energy \( (E) \) plotted against the extent of conversion rate \( (\alpha) \)

The average apparent activation energy data calculated from the slopes of the Arrhenius plots by the two models is shown as a function of conversion (Figure 2.5). The activation energy values from the Friedman and DAEM methods showed the same trends and increased essentially only above the conversion rate of 0.6. The similar results were reported in the study of natural fibers (Yao et al., 2008). The differential Friedman method gave an average activation energy value of 107 kJ/mol in the conversion range of 0.1-0.6, while the DAEM method led to an average value of 85 kJ/mol within the same conversion range. The value by the Friedman method was higher than the one by the DAEM method. It was suggested that different kinetics analysis methods were complementary rather than competitive (Brown et al., 2000). Thus, an appropriate activation energy range should be acquired by applying different methods. Consequently, the general activation energy range of 80-110 kJ/mol was obtained for the thermal decomposition of the tar in the \( \text{N}_2 \) atmosphere. This was within activation energy range (60-170 kJ/mol) from a variety of biomass (Di Blasi, 2002; Grønli et al., 2002; Kumar et al., 2008). As mentioned above, the reaction mechanism changed when the conversion rate was larger than 0.6,
which resulted in the complexity of modeling the entire thermal decomposition process of the tar. Therefore, this study focused on the conversion range of 0.1-0.6, within which the decomposition of main components completed during the aforementioned temperature range from 183 to 252 °C. By this way, the degradation process of the tar was simplified, which was quite meaningful for understanding the thermal properties of tar derived materials.

2.4 CONCLUSIONS

In this study, a comprehensive analysis of chemical composition and thermal degradation of the tar from corn stover gasification was carried out. The tar was a complex mixture mainly composed of highly branched PAHs, furans, aliphatics, and esters as indicated by the GC-MS and FTIR spectroscopy. The elemental analysis showed that biomass tar with higher H/C and O/C was more oxygenated and less aromatic than fossil pitches, implying that the tar was more reactive. The complex composition of the tar led to a broad thermal decomposition temperature range. The tar decomposed at a low temperature (183-252 °C depending on the heating rates) compared with biomass feedstock, due to the low molecular mass components in the tar produced by gasification. The thermal decomposition kinetics of the tar indicated that single reaction mechanism can be applied at low conversion and the reaction mechanism changed at higher conversions caused by the complex reactions in decomposition process of biomass tar. The tar decomposition was simplified by focusing on the conversion range of 0.1-0.6 and a general activation energy range of 80-110 kJ/mol by the two models. The simplified approach is helpful for better understanding the thermal properties of tar derived materials and facilitating its further processing and utilization.
2.5 REFERENCES


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CHAPTER 3 FABRICATING ELECTROSPUN NANOFIBER WITH ANTIMICROBIAL CAPABILITY: A FACILE ROUTE TO RECYCLE BIOMASS TAR

3.1 INTRODUCTION

Energy shortage, environmental pollution, and global warming are crucial issues that drive us to utilize renewable natural resources in a more sustainable way. Biomass and biofuels are promising alternatives to petroleum-derived materials and energy due to their unique characteristics including abundance, renewability, and carbon neutrality. Thermochemical transformations such as pyrolysis and gasification can convert biomass into biofuels (Vassilev et al., 2010). However, tar (heavy hydrocarbons) is always produced as a by-product from biomass thermochemical conversion processes (Di Marcello et al., 2014). The tar needs to be removed from the producer gas to avoid operational problems associated with clogging in downstream units and the poisoning of catalysts in end-use applications (Tuomi et al., 2015). The disposal of tar can cause environmental pollution due to its high resistance to degradation (Li and Suzuki, 2010), and the current treatments focus on tar reforming processes using steam and catalysts (Wang et al., 2013; Widayatno et al., 2014). However, these processes are quite complex and costly. Therefore, comprehensive separation and utilization technologies for biomass tar are needed for sustainable application of biomass, biofuels, and valued-added chemicals, and to expand the scope of biomass utilization.

Considering its high carbon content, it should be possible to utilize biomass tar as a carbon-based feedstock. Tar is a complex mixture of hydrocarbons, including single ring to five-ring polycyclic aromatic hydrocarbons (PAHs) along with other oxygen-containing hydrocarbons

such as polyphenols (Li and Suzuki, 2009; Rice et al., 2011). Tar from biomass gasification is mainly composed of phenols, aromatics, furans, aliphatics, and esters (Song et al., 2015; Yu et al., 2014). Elemental analysis showed that the tar with higher H/C and O/C was more oxygenated and less aromatic than fossil pitches, implying that the tar was more reactive (Song et al., 2015). The components of the tar can be extracted to use as valuable substitutes for petroleum derived chemicals. In the past, a larger number of chemicals such as anthracene, acenaphthene, pyrene, phenol, and most of heterocyclic aromatic compounds were extracted from coal tar, but the procedures for separation and purification were quite complex (Amen-Chen et al., 1997; Li and Suzuki, 2010). Accordingly, it is much more practical and cost-effective to utilize tar as a whole. Using the entire tar or pitch, carbon fibers and carbon foams were fabricated and utilized as adsorption or filtration medium due to their large surface areas and high porosities (Bui et al., 2009; Li et al., 2011). However, most previous research focused on using tar or pitch from coal and petroleum, and little attention was paid to the utilization of tar from biomass. Limited attempts were made to use wood tar as preservatives for wood and as a component in phenol-formaldehyde resin formulation in plywood adhesives (Lu and Wu, 2013; Suzuki et al., 1997). However, no study has been carried out so far to manufacture fibrous materials using tar from biomass thermochemical conversions.

Among the fiber fabricating techniques, electrospinning has emerged as a simple and highly versatile method to prepare multifunctional fibers from a remarkable range of organic and inorganic materials (Reneker and Yarin, 2008). For typical electrospinning, the spinning solutions or suspensions are ejected from the needle tip under the driving force of high voltage. During the travel of the electrospun jet from a needle tip to a grounded collector, the solvent evaporates and ultrafine fibers form and are deposited on the collector. Owing to their desirable
characteristics including small width, large specific surface area, multi-scale porosity, and high flexibility for surface functionalization, these electrospun nanofibers have wide applications in adsorption, filtration, optoelectronics, sensors, tissue engineering, and antimicrobial materials (Greiner and Wendorff, 2007). Some industrial products such as filtration and purification films are produced by electrospinning, and continuous efforts have been made to optimize the electrospinning process (Persano et al., 2013). Electrospun fibers have been produced from petroleum-based isotropic pitch dispersed in tetrahydrofuran (THF) (Park et al., 2003; Park et al., 2004). However, these fibers were beaded due to a low solution viscosity, resulted from the low molecular weight and solubility of the tar in solvents. This problem can be resolved by blending tar or pitch with a polymer such as polyacrylonitrile (PAN) (Bui et al., 2009). Combining the outstanding electrospinnability of PAN and the variety of surface functional groups found in tar enables fabrication of continuous electrospun nanofibers with varying functionalities.

In this study, functional nanofibers were prepared by electrospinning tar/PAN suspensions. The electrospinnability of the tar/PAN suspensions and the properties of the resultant nanofibers with varying tar contents were investigated. The electrospun nanofibers were characterized by field emission scanning electron microscopy (FE-SEM), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, thermal gravimetric analysis (TGA), and N₂ adsorption/desorption measurements. Additionally, antimicrobial activities of the electrospun nanofibers were tested against Gram-positive S. aureus and Gram-negative E. coli bacteria.

3.2 MATERIALS AND METHODS

3.2.1 Materials

Tar was produced from the gasification of corn stover at 500-600 °C in the Xigou Biomass Fuel Gas Plant, Shanxi, China. The collected tar material was dried in a vacuum oven at 80 °C.
for at least 48 h to remove water. The dried tar was placed in a sealed container for further
treatment. Polyacrylonitrile (PAN, $M_w = 150,000$ g/mol) and $N, N$-dimethylformamide (DMF)
were supplied by Sigma-Aldrich (St. Louis, MO, USA).

3.2.2 Electrospinning Solutions/Suspensions

PAN powder (1 g) was mixed with DMF (9 g) and vigorously stirred overnight at room
temperature to obtain a homogenous solution. Meanwhile, the dried tar powder was dispersed in
DMF under vigorous magnetic stirring for at least 24 h. The as-prepared PAN solution and tar
suspensions were mixed and transferred to an ultrasonic bath, further dispersing the tar for 30
min, to create the final electrospinning tar/PAN suspensions. The suspensions with the addition
of 30, 50, and 100 wt% tar based on PAN by weight were designated as 30Tar/PAN, 50Tar/PAN
and 100Tar/PAN, respectively (numbers representing relative weight percentage of tar to PAN in
the suspensions).

Conductivities of the prepared solutions and suspensions were determined using an Oakton
PC700 pH/mV/Conductivity/°C bench meter (Oakton Instruments, Vernon Hills, IL, USA).
Shear viscosities were measured by a rheometer (AR2000ex, TA Instruments, New Castle, DE,
USA). A 40 mm cone-plate geometry with a cone angle of 1 °59′42″ and a truncation of 56 μm
was used for the viscosity measurements. The viscosities were measured at shear rates ranging
from 0.1 to 1000 s$^{-1}$ at 25 °C. To avoid evaporation of solvent during testing, a solvent trap cover
was used to seal the 56 μm gap between cone and parallel plate and the moat on the top of the
cover was filled with low-viscosity silicon oil.

3.2.3 Fabrication of Electrospun Tar/PAN Nanofibers

The prepared precursor solution or suspension was transferred into a 5 mL glass syringe
with a 0.413 mm inner diameter stainless steel needle (Figure 3.1). The needle was connected to
a high voltage power supply (Gamma High Voltage Research, Ormond Beach, FL, USA), which generated a positive DC Voltage of 15 kV. The solution or suspension was fed at a flow rate of 0.5 mL/h by a syringe pump (Chemyx Fusion 100, Stafford, TX, USA). A piece of grounded aluminum foil, placed at a horizontal distance of 20 cm from the needle tip, was used to collect ultrafine electrospun nanofibers at a relative humidity of 60% and a temperature of 25 °C. The nanofibers so obtained were dried in a vacuum oven at 60 °C to remove the residual solvent (DMF) and then sealed for storage prior to structure and property analysis.

Figure 3.1 Schematic illustrating the process for fabricating biomass tar/PAN nanofibers by electrospinning

3.2.4 Characterizations

Surface morphologies of the neat PAN and tar/PAN nanofibers were observed with a field emission scanning electron microscope (FE-SEM, FEI QuantaTM 3D FEG Dual Beam SEM/FIB, Hillsboro, OR, USA) at 10 kV. Each specimen was coated with a thin layer of gold prior to the FE-SEM observation. The distribution of the nanofiber diameters was obtained by analysis of FE-SEM micrographs using image processing software (Image J 1.46r). One hundred individual nanofibers were randomly measured from each image, and the average and standard deviation values were obtained.
Fourier transform infrared (FTIR) spectra of the nanofibers were collected using a Bruker FTIR spectrometer (Alpha, Bruker Optics Inc., Billerica, MA, USA) in attenuated total reflectance (ATR) mode. Each spectrum between 4000 and 600 cm\(^{-1}\) was recorded by accumulation of 64 scans with a spectral resolution of 4 cm\(^{-1}\). The absorption band at 2243 cm\(^{-1}\), due to the C≡N stretching vibration, was used for spectrum normalization. This absorption band was assumed to be essentially unaltered in the electrospun PAN and tar/PAN nanofibers.

The thermal decomposition of the nanofibers was investigated by thermogravimetric analysis (TGA, TA Q50 analyzer, TA Instruments, New Castle, DE, USA), with a resolution of 0.1 μg. Samples of 5-10 mg were heated from 30 to 600 °C at a rate of 10 °C/min. The measurements were carried out under a N\(_2\) atmosphere at a flow rate of 60 mL/min. Differential scanning calorimetry (DSC) measurements were performed with a TA Q200 system under a nitrogen atmosphere at a flow rate of 60 mL/min. Each sample with an approximate weight of 5 mg was scanned from 40 to 350 °C at a heating rate of 10 °C/min.

The porosity of the electrospun neat PAN and tar/PAN nanofibers was calculated through the following equation (Xu et al., 2007):

\[
\text{Porosity } \% = \frac{(\rho_0 - \rho)}{\rho_0} \times 100
\]

where \(\rho_0\) and \(\rho\) (g/mL) are the densities of cast film and electrospun nanofiber, respectively. The film samples were cast from a PAN solution and tar/PAN suspensions in Petri dishes followed by evaporation and further vacuum drying at 80 °C overnight.

The nitrogen adsorption and desorption isotherms were determined using a Quantachrome Autosorb-1 porosimeter (Boynton Beach, FL, United States) at 77 K, in order to determine the intra-fiber porosity and pore size distribution of the electrospun nanofibers. Prior to the adsorption measurements, each sample of 1 g was outgassed at 353 K under vacuum until a
stable pressure (<0.04 mmHg) was obtained. The specific surface area was determined from the nitrogen adsorption branch of the isotherm by the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). The intra-fiber pore size distribution was determined from the nitrogen desorption branch according to the Barrett-Joyner-Halenda (BJH) method (Barrett et al., 1951).

Antimicrobial activity of the as-spun neat PAN and tar/PAN nanofibers was tested against both Gram-positive *S. aureus* and Gram-negative *E. coli* by viable cell counting methods. *S. aureus* and *E. coli* were cultivated in sterilized Tryptic Soy Broth and then incubated overnight at 37 °C with a shaking incubator. Culture medium (1 mL) was diluted with 9 mL of sterilized broth solution. The as-spun nanofibers (25 mg) were immersed into the diluted culture suspension (5 mL). After 24 h incubation and shaking at 37 °C, different dilutions (10⁻¹ to 10⁻⁵) were made by successively adding 1 mL culture into 9 mL of broth solution. Then, 0.2 mL of the diluted culture was spread on an agar plate and incubated at 37 °C for 24 h. The number of colonies was counted and three repeats were performed for each sample. The antimicrobial capability of the tar/PAN fibers was defined as follows:

$$\text{Antimicrobial} \% = \left( \frac{A-B}{A} \right) \times 100 \quad (3.2)$$

where $A$ and $B$ are the number of colonies (colony forming unit, CFU/mL) before and after the electrospun nanofibers were added, respectively.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Characteristics of Electrospinning Solutions

The properties of precursor solution or suspensions including conductivity, viscosity, and concentration are important parameters in determining microstructure of the electrospun nanofibers. DMF was selected for preparing the precursor solutions/suspensions because it was an excellent solvent for PAN and also a good dispersing agent for biomass tar. Homogeneous
PAN solutions and tar/PAN suspensions were prepared, and conductivities and viscosities were measured. The values of conductivity were 55.7, 59.9, 61.4, and 65.8 μS/m for PAN, 30Tar/PAN, 50Tar/PAN, and 100Tar/PAN, respectively. The improved conductivity with respect to the increased tar content could be attributed to the presence of the polar functional groups of the tar components, such as hydroxyl, carboxyl, carbonyl, and ethers (Song et al., 2015). Similar findings were obtained when polar materials were blended with polymers in electrospinning solutions (Chen et al., 2013; Zhou et al., 2011). The increased conductivity promoted more continuous spinning of smaller diameter and bead-free fibers, because of the increased charge density in the electrospinning jets (Greiner and Wendorff, 2007). However, the conductivity alone does not determine the morphology of the electrospun nanofibers.

![Figure 3.2 Variations of apparent viscosity with shear rates for PAN solutions and tar/PAN suspensions](image)

Shear viscosities of PAN solutions and tar/PAN suspensions at a shear rate range of 0.1-1000 s\(^{-1}\) are shown in Figure 3.2. The PAN solution was basically a Newtonian fluid at low shear rates (0.1-100 s\(^{-1}\)). At greater than 100 s\(^{-1}\), the viscosity of the PAN solution decreased with an
increase of shear rates, exhibiting a typical pseudoplastic behavior resulting from a gradual removal of chain entanglements with increased shear stress (Zhou et al., 2011). Compared to the PAN solution, the viscosities of the tar/PAN suspensions were greatly decreased at all shear rates, although the near Newtonian behavior at the lower shear rates persisted, except for 100Tar/PAN. For this sample with equal weights of tar and PAN, the viscosity at the lower shear rates was only slightly lower, but the shear-thinning behavior began almost immediately. The viscosity decrease can be attributed to further disruption of PAN chain-chain interactions (entanglements) by the tar, making the PAN molecules much easier to align. The low molecular weight tar essentially acted as a swelling agent (plasticizer). On the other hand, the increased viscosities obtained upon increasing the tar content can be attributed to contributions from the non-swelling tar components of higher viscosity than DMF. It was well known that electrospinning solutions or suspensions are subjected to very high shear rates when flowing through a steel needle. Thus the PAN solutions and tar/PAN suspensions were even less viscous during the electrospinning process.

3.3.2 Microstructure of Electrospun Fibers

Surface morphologies of the electrospun PAN and tar/PAN nanofibers are shown in Figure 3.3. The tar suspension without PAN in DMF was not electrospinnable, forming discrete droplets rather than continuous fibers. This was due to the low molecular weights of the tar components, which resulted in non-viscous and non-elastic fluid behavior. At such a low viscosity, the viscoelastic stress in the electrospun jet was not strong enough to counter the high Coulombic forces and high surface tension. The blending of the biomass tar with PAN allowed electrospinning of continuous nanofibers to take place due to the excellent electrospinnability of PAN. Nearly homogenous fibers without any beads were randomly deposited on the grounded
collector (Figure 3.3). However, it was noted that some bulges appeared on the surface of the electrospun nanofibers as the tar content increased (Figure 3.3D), due to aggregation of the tar. A further increase in the tar content of the blends made continuous fiber spinning quite difficult. Consequently, one hundred percent of the tar based on PAN by weight represented the largest tar fraction that could be used to make continuous electrospun nanofibers. In addition, some surface pits or dents were present on the rough surfaces of the electrospun nanofibers, observed from the inset photos at a higher magnification (Figure 3.3). This was due to the rapid evaporative cooling of the solvent that occurred when the electrospinning jet was being propelled toward the collector (Park et al., 2004). Furthermore, the surfaces of the tar/PAN nanofibers became much rougher than the PAN nanofibers, especially for the 100Tar/PAN. This could be caused by some phase separation between the tar and PAN when the solvent evaporated.

![Figure 3.3 FE-SEM micrographs of the electrospun nanofibers (inserted photos are at higher magnification) A PAN; B 30Tar/PAN; C 50Tar/PAN; D 100Tar/PAN](image)

Figure 3.3 FE-SEM micrographs of the electrospun nanofibers (inserted photos are at higher magnification) A PAN; B 30Tar/PAN; C 50Tar/PAN; D 100Tar/PAN
Although the addition of tar had little effect on the surface morphology of the PAN nanofibers, it influenced the average diameter of the nanofibers (Figure 3.4). The average diameter of nanofibers from solutions of PAN in DMF was 422 nm. The diameters of tar/PAN composite nanofibers increased continuously with respect to tar content, up to 948 nm at 100 wt% tar loading level. The increased concentrations of the electrospinning suspensions with additional tar content contributed to these larger nanofiber diameters, and the effect was probably larger than those from the increased conductivity and decreased viscosity. Additionally, the size uniformity of tar/PAN fibers at 30 and 50 wt% tar loading levels was better than that of fibers with the largest tar content (Figure 3.4). This can be mainly attributed to the aggregation of tar and the phase separation mentioned above, which became more obvious for 100Tar/PAN.

### 3.3.3 ATR-FTIR Spectra of Electrospun fibers

ATR-FTIR spectra of the PAN and tar/PAN nanofibers were collected (Figure 3.5). Characteristic absorbance peaks for the PAN nanofibers were observed, including the CH\textsubscript{2} asymmetrical and symmetrical stretching vibrations at 2929 and 2869 cm\textsuperscript{-1}, the intense CN stretch at 2243 cm\textsuperscript{-1}, CH\textsubscript{2} bending at 1450 cm\textsuperscript{-1}, CH\textsubscript{2} wagging at 1364 cm\textsuperscript{-1}, CH wagging at 1248 cm\textsuperscript{-1}, and the skeletal vibration of the PAN backbone at 1070 cm\textsuperscript{-1} (Arshad et al., 2011; Coleman
The bands at 1664 cm\(^{-1}\) appeared as a result of impurities in the polymer (Liang and Krimm, 1958). For the tar/PAN nanofibers, aside from the absorption peaks of PAN, additional absorption bands characteristic of the tar compounds appeared, namely OH stretching (3359 cm\(^{-1}\)), carbonyl stretching (1701 cm\(^{-1}\)), aromatic skeletal vibrations (1609 and 1507 cm\(^{-1}\)), asymmetrical stretching of ethers (1113 cm\(^{-1}\)), and C-H out-of-plane bending of aromatics (828 and 760 cm\(^{-1}\)). These peaks are typical of IR absorption in phenols, acids, ketones, aromatics, and ethers in the tar (Song et al., 2015), and they were not present in the PAN nanofibers. In addition, the absorption peaks of the tar components showed increased intensities with increased tar content in the nanofibers. The bands at 2929, 2869, and 1450 cm\(^{-1}\) which were ascribed to CH\(_2\) absorption from both PAN and tar also showed increased intensity with increased addition of tar. All of these findings confirmed that the tar was successfully incorporated into the tar/PAN electrospun nanofibers.

![Figure 3.5 The ATR-FTIR spectra of the PAN, 30Tar/PAN, 50Tar/PAN, and 100Tar/PAN electrospun nanofibers](image-url)

Figure 3.5 The ATR-FTIR spectra of the PAN, 30Tar/PAN, 50Tar/PAN, and 100Tar/PAN electrospun nanofibers
3.3.4 Thermal Properties

Figure 3.6 shows comparisons of measured TG and DTG curves of the PAN nanofibers, tar/PAN composite nanofibers, and the original tar. The as-spun PAN nanofibers showed three main weight loss stages. In the first stage (up to 285 °C), there was only a slight weight loss. In the second stage, rapid PAN decomposition with a 30% weight loss occurred in a temperature range from 285 to 315 °C. This weight loss was due to the side chain degradation of the PAN polymer with release of volatile gases (Chatterjee et al., 1995; Xue et al., 1997). A further decrease of weight (from 70 to 42%) over a broad temperature range of 315-460 °C in the third stage was mainly caused by decomposition of the carbon-carbon main chain (Chen et al., 2013). Further heating up to the 600 °C did not lead to any significant additional weight loss.

The tar/PAN composite nanofibers showed an overlap of the mass losses of tar and PAN. Compared with the neat PAN fibers, it was clearly seen that the tar/PAN nanofibers began to lose weight at a lower temperature because of the lower decomposition temperature of some tar components (Table 3.1 and Figure 3.6). The pure tar started to degrade rapidly at a temperature
of about 150 °C, at which point the mass loss was 5 wt%. Therefore, the weight loss of the 
tar/PAN nanofibers in the first stage (up to 280 °C) can be ascribed completely to the degradation 
of tar components. Further weight loss of the tar/PAN nanofibers was mainly due to the 
decomposition of the PAN polymer. Additionally, the thermal stability of the tar/PAN nanofibers 
decreased slightly with an increased addition of tar components. At 600 °C, a 35 wt% residue 
was observed for the tar/PAN composite nanofibers. Considering the comparable residual 
weights of the tar/PAN and the PAN nanofibers, it was suggested that biomass tar be used as 
precursor materials to manufacture carbon nanofibers. The future demand for carbon nanofibers 
will increase significant and alternative raw materials must be identified and implemented to 
reduce their price (Frank et al., 2014). Therefore, biomass tar can be a cheaper precursor for 
producing low-cost carbon nanofibers. Further investigations need to be done in this area with 
regard to the complicated composition and low thermal stability of the tar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_{10%}\textsuperscript{a} (°C)</th>
<th>T_{50%}\textsuperscript{a} (°C)</th>
<th>Residue (%)</th>
<th>T_{cyc}\textsuperscript{b} (°C)</th>
<th>ΔH_{cyc}\textsuperscript{c} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>285</td>
<td>420</td>
<td>38</td>
<td>308</td>
<td>376</td>
</tr>
<tr>
<td>30Tar/PAN</td>
<td>223</td>
<td>411</td>
<td>36</td>
<td>292</td>
<td>394</td>
</tr>
<tr>
<td>50Tar/PAN</td>
<td>219</td>
<td>410</td>
<td>36</td>
<td>290</td>
<td>399</td>
</tr>
<tr>
<td>100Tar/PAN</td>
<td>195</td>
<td>408</td>
<td>35</td>
<td>286</td>
<td>439</td>
</tr>
</tbody>
</table>

\textsuperscript{a} T_{10\%}, T_{50\%}, the temperature corresponding to 10, 50 wt% of weight loss; 
\textsuperscript{b} T_{cyc}, cyclization temperature; 
\textsuperscript{c} ΔH_{cyc}, heat of cyclization.

The DSC for the PAN nanofibers showed a strong exothermic peak at 308 °C (Table 3.1, 
Figure 3.7), which is attributed to the cyclization of the nitrile groups of PAN (Sui et al., 2013; 
Wu et al., 2012). However, the cyclization of PAN in the tar/PAN nanofibers differed from that 
in the neat PAN nanofibers. With an increased content of tar in the electrospun fibers, the
cyclization temperature \( T_{\text{cyc}} \) shifted toward lower temperatures and the heat of cyclization \( \Delta H_{\text{cyc}} \) increased. This altered reaction behavior upon addition of tar resulted from the catalytic action and reactions of the hydroxyl groups of phenolic compounds and the acid groups of carboxylic acids that were constituents of the biomass tar. The cyclization of PAN during heating could be initiated or catalyzed by these ionizable groups (Kim et al., 1993). The hydroxyl or acid groups of the tars located at the PAN interfaces acted catalytically, lowering the reaction’s activation energy and thus decreasing \( T_{\text{cyc}} \) (Figure 3.7). The increasing \( \Delta H_{\text{cyc}} \) indicated a higher conversion of C≡N groups in the cyclization reaction, also consistent with the presence of catalytically active functional groups. Alternatively, it was reported that a lower cyclization temperature of PAN might be due to the better chain orientation on the molecular level (Gu et al., 2005; Zhang et al., 2010). Thus, the lower \( T_{\text{cyc}} \) and higher \( \Delta H_{\text{cyc}} \) of the tar/PAN nanofibers were also resulted from the plasticizing effects of the tars, facilitating the orientation of PAN molecular chains during the electrospinning processes.

![Figure 3.7 DSC of the PAN (solid curves) and tar/PAN fibers (dotted curves). The inset shows a schematic of a tar-initiated PAN cyclization reaction (Ar-OH indicates a phenolic component of the tar).](image-url)
3.3.5 Surface Area and Porosity

Both intra- and inter-fiber pores existed in the electrospun nanofibers. The intra-fiber pores of the neat PAN and tar/PAN nanofibers were investigated by nitrogen adsorption/desorption measurements at 77 K. The isotherms of the electrospun fibers are somewhat similar to a type IV adsorption process with a hysteresis loop at high P/P₀ (Figure 3.8), indicating that a mesopore structure exists (Sing et al., 1985). Similar mesopore characteristics were found in electrospun nanofibers from cellulose reinforced polyacrylamide (Zhou et al., 2013). The isotherms of the neat PAN and tar/PAN nanofibers showed similar hysteresis loops. The difference between the adsorption and desorption branches at low P/P₀ indicated that the swelling of the polymer opened up new micropores during the course of the measurement. Such swelling was a common phenomenon in certain polymeric adsorbents, but its occurrence here demonstrated that for adsorbates with greater attraction to certain functional groups of the tar, and additional surface area could be created above the characteristic value of pure PAN (which was resistant to most organic solvents, with a Tg of 85 °C).

![Figure 3.8 Nitrogen adsorption/desorption isotherm at 77 K and BJH pore size distribution (inset) of the PAN nanofibers. Dv(d) is the derivative of pore volume with respect to pore diameter](image-url)
The inset of Figure 3.8 shows the pore size distribution. The diameters of the neat PAN fibers were mainly between 1-27 nm, confirming the predominantly mesoporous structure. The calculated surface area, total pore volume, and average pore diameters from the isotherms of the electrospun fibers are shown in Table 3.2. The tar/PAN nanofibers exhibited lower BET surface areas and total pore volumes, compared to the neat PAN nanofibers. The average pore diameter of the tar/PAN nanofibers showed an increasing trend with increasing tar content, consistent with swelling of the PAN by the tar.

The total porosity of the electrospun nanofibers, representing the sum of the contributions from the larger inter-fiber voids and the intra-fiber pores, was obtained by calculating the densities of the as-spun nanofibers and the corresponding cast films (Table 3.2). The average porosity of the neat PAN nanofibers was 63%. The porosity decreased to 61%, 58% and 51% with an addition of 30, 50, and 100 wt% tar, respectively. The decreased average porosity of the tar/PAN composite nanofibers was consistent with increased fiber diameters. Due to the inter- and intra-fiber pores and high specific surface area of the tar/PAN electrospun nanofibers, they can be considered in the applications of adsorption of hazardous gas or heavy metals for environmental protection.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
<th>Total porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>14</td>
<td>0.020</td>
<td>5.6</td>
<td>63</td>
</tr>
<tr>
<td>30Tar/PAN</td>
<td>12</td>
<td>0.019</td>
<td>6.2</td>
<td>61</td>
</tr>
<tr>
<td>50Tar/PAN</td>
<td>12</td>
<td>0.018</td>
<td>5.7</td>
<td>58</td>
</tr>
<tr>
<td>100Tar/PAN</td>
<td>10</td>
<td>0.017</td>
<td>7.1</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 3.2 Morphological characteristics of the neat PAN and tar/PAN nanofibers
3.3.6 Antimicrobial Activity

Figure 3.9 Antibacterial activity of the neat PAN and tar/PAN nanofibers against *S. aureus* (A, B, and C) and *E. coli* (D, E, and F). (A) and (D): PAN; (B) and (E): 50Tar/PAN; (C) and (F): 100Tar/PAN

The effects of the tar/PAN electrospun nanofibers on the growth of the bacteria *S. aureus* and *E. coli* are shown in Figure 3.9. The counted numbers of bacterial colonies in the diluted bacteria suspensions decreased after the tar/PAN nanofibers were used, while the neat PAN nanofibers showed no effect on the growth of the bacteria. An increase in the tar content of the electrospun nanofibers helped improve the broad-spectrum antimicrobial activities against *S. aureus* and *E. coli*. The calculated antimicrobial capability values of 30Tar/PAN, 50Tar/PAN and 100Tar/PAN nanofibers against *S. aureus* were (8±2)%, (19±3)%, and (36±7)%, respectively, while the values of corresponding nanofibers against *E. coli* were (9±3)%, (17±4)%, and (39±6)%, respectively. The antimicrobial capability of the tar/PAN nanofibers was attributed to the action of the phenolic components in the biomass tar. It was reported that phenolic compounds affected the growth and metabolism of bacteria by adsorbing on cell membranes, interacting with enzymes, and disturbing cell membrane permeability (Medina et al., 2006;
Pereira et al., 2007; Vaquero et al., 2007). The phenolic compounds diffused slowly into the broth and inhibited the growth of the bacteria. Thus, the larger content of tar in the electrospun nanofibers offered more phenolic compounds diffusing into the broth, leading to improved antimicrobial capability with lower colony forming units of the bacteria. In addition, the porous characteristics of electrospun fibers resulted in an increased surface area, which was helpful for antimicrobial efficacy through increased exposure of phenolic compounds to the surrounding bacteria. Electrospun polymer nanofibers loaded with silver nanoparticles were used in numerous applications such as wound dressing (Rujitanaroj et al., 2008) and tissue scaffolds (Xing et al., 2010). Compared with silver nanoparticles, biomass tar showed lower antimicrobial efficacy mainly due to the lower quantities of phenolic compounds that could diffuse into the broth solution. However, biomass tar is a much cheaper additive than silver nanoparticles and can largely reduce the cost of antimicrobial materials. The antimicrobial efficacy of biomass tar can be improved by further manipulating the composition and concentration of phenolic compounds in the tar-derived electrospun nanofibers.

3.4 CONCLUSIONS

With the goal of utilizing biomass tar to the greatest extent, variable tar amounts were blended with PAN prior to electrospinning. The contents of tar significantly affected the morphology, thermal properties, pore characteristics, and antimicrobial activity of the resulting electrospun nanofibers. Continuous nanofibers were produced at the tar content levels up to 100 wt% based on the weight of PAN. The tar/PAN nanofibers exhibited increased average diameters and surface roughness with increasing content of tar. ATR-FTIR spectroscopy revealed that the tar was successfully incorporated into the tar/PAN nanofibers. The tar/PAN nanofibers were less thermally stable than the neat PAN nanofibers due to the relatively low onset temperature of
degradation of biomass tar, and their thermal stability decreased with increasing amount of tar. However, the tar/PAN nanofibers had a comparable amount of residual weight (35%) compared to PAN (38%) at 600 °C, suggesting that tars can be an attracting precursor for manufacturing carbon nanofibers. Furthermore, the addition of tar facilitated catalytically the cyclization of PAN, which is helpful for stabilization processes in the manufacture of PAN-based carbon fibers. The tar/PAN nanofibers exhibited increased antimicrobial capacity against \textit{S. aureus} and \textit{E. coli} with increased tar content. This study provides a sustainable and economical way to recycle biomass tar and can help improve the economics of biofuel production and reduce associated environmental contamination.

3.5 REFERENCES


CHAPTER 4 POROUS CARBON NANOFIBERS FROM ELECTROSPUN BIOMASS TAR/POLYACRYLONITRILE/SILVER HYBRIDS AS ANTIMICROBIAL MATERIALS

4.1 INTRODUCTION

Carbon nanofibers (CNFs) with diameters in the submicron and nanometer range have attracted an increasing attention due to their superior chemical, electrical, and mechanical properties (Gardea et al., 2013; Morgan, 2005; Zhang et al., 2014). Among various CNFs, porous CNFs exhibit promising applications in energy conversion and storage, gas adsorption, and biomedical fields, attributed to their ultrahigh specific surface area and porosity (Aykut, 2012; Wang et al., 2013; Xu et al., 2013). The future demand for porous CNFs with diverse functionalities is expected to increase significantly and alternative raw materials have to be identified and implemented to reduce their production cost. Renewable raw materials from biomass sources are attractive for producing low-cost CNFs with minimal environmental impact, due to their unique characteristics including abundance and renewability (Wu et al., 2013; Xu et al., 2014).

Tar, an industrial by-product from biomass pyrolysis or gasification, is a potential source for producing such low-cost CNFs (Song et al., 2015b). Currently, tar is treated as an industrial waste, and its disposal is extremely difficult and costly due to its complex chemical composition and high resistance to biodegradation. Current efforts focus on tar reforming processes using steam or catalysts (Guan et al., 2013; Li et al., 2014), but these treatments are quite complicated, costly, and time-consuming. Our previous study indicated that biomass tar mainly contained phenols and aromatics originated from lignin decomposition during pyrolysis or gasification.

processes, and presented a high carbon content (i.e., over 75%) (Song et al., 2015b). Thus, the biomass tar can be a promising low-cost precursor for manufacturing CNFs. Tar or pitch derived from coal and petroleum was successfully processed into carbon fibers with a high specific surface area and porosity (Derbyshire et al., 2001; Kim et al., 2013). However, no reports of CNFs based on tar from biomass conversions have been found. It is thus of significant practical interest to utilize biomass tar as a low-cost precursor for carbon materials instead of disposing it as a waste causing environmental pollutions.

CNFs are commonly produced through preparations of precursor fibers followed by thermo-oxidative stabilization and carbonization processes (Frank et al., 2014). Although traditional spinning methods such as wet spinning and melt spinning have been used to manufacture precursor fibers, electrospinning emerges as a simple and highly versatile approach to fabricate multifunctional nanofibers with diameters down to a few nanometers (Matsumoto et al., 2013; Reneker and Yarin, 2008). Various polymeric materials including polyacrylonitrile (PAN), cellulose, and pitch are electrospun into precursor nanofibers, and diversified CNFs are obtained with subsequent stabilization, activation, and carbonization treatments (Joshi et al., 2010; Zhang et al., 2014). The small dimension of electrospun CNFs creates a larger specific surface area, compared to CNFs from traditional spinning methods (Inagaki et al., 2012). Nevertheless, technical difficulties emerge from complex compositions of tar when it is used for electrospinning. Tar is composed of a number of mixed substances, which cannot be dissolved by solvents completely. Furthermore, most components of tar have relatively low molecular weights. Thus, precursor suspensions prepared by tar exhibit inadequate homogeneity and low viscosity, which is detrimental for producing smooth and continuous electrospun fibers. Consequently, it is hard to obtain tar-based electrospun nanofibers with uniform diameters and
beaded or dumb-bell shaped fibers were usually produced (Park et al., 2004; Park and Jang, 2003). However, the electrospinning ability of tar can be improved by blending it with a polymer such as PAN with excellent electrospinning ability. The mixture of petroleum derived pitch and PAN was successfully electrospun into continuous fibers, and activated carbon fibers with a high specific surface area ranging from 732 to 1877 m²/g were prepared through subsequent stabilization, carbonization, and steam activation processes (Bui et al., 2009). It is noteworthy that tar derived CNFs may not be able to perform well in high strength applications due to structural heterogeneity of tar, and efforts have been made to enhance their mechanical properties by modifying compositions and molecular structures of tar (Kim et al., 2014). Nevertheless, tar can be used to fabricate electrospun CNFs with various functionalities such as antimicrobial capacity by incorporating silver nanoparticles (Li et al., 1998).

The aim of this study was to fabricate porous CNFs with antimicrobial capabilities from recycled biomass tar as low-cost precursor by electrospinning and subsequent stabilization and carbonization processes. Suspensions of biomass tar, PAN, and silver nanoparticles were prepared and electrospun into precursor nanofibers that were further converted to porous CNFs by oxidative stabilization and carbonization in an inert atmosphere. The effects of tar loading levels on electrospinning ability of suspensions, morphologies, chemical structures, thermal properties, pore features, and antimicrobial performance of resultant CNFs were investigated.

4.2 MATERIALS AND METHODS

4.2.1 Materials

Tar was collected from the gasification of corn stover at 500-600 °C in Xigou Biomass Fuel Gas Plant, Shanxi, China. Water in the tar was removed by drying in a vacuum oven at 80 °C for at least 48 h. The dried tar was then stored in a sealed container for further processing.
PAN $(M_w = 150,000 \text{ g/mol})$, $N, N$-dimethylformamide (DMF), and silver nitrate ($\text{AgNO}_3$) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

4.2.2 Fabrication of Carbon Fiber Precursors

PAN was added in DMF and mixed using a magnetic stirrer for 24 h at room temperature. A certain amount of dried tar powder was dispersed in DMF under vigorous magnetic stirring for at least 24 h at room temperature. The PAN solution and tar suspension in DMF were blended and the mixture was transferred to an ultrasonic bath to further disperse the tar in the blend for 30 min. The concentration of PAN in the mixture was fixed at 10 wt%. The loading levels of tar were 0, 50, and 100 wt% with respect to weight of PAN (Table 4.1). Silver nitrate powder was then added into the prepared tar/PAN suspensions (molar ratio of $\text{AgNO}_3$ and repeating unit of PAN was 1/10). The resultant suspensions were shielded from light, and stirred for 2 h in an ice bath to ensure complete dissolution of silver nitrate. Afterwards, silver ions were reduced to silver nanoparticles by heating the suspensions to 90 °C in a water bath and holding at this temperature for 15 min. Finally, the suspensions containing tar, PAN, and silver nanoparticles were cooled down to room temperature prior to electrospinning.

Table 4.1 Compositions and carbon yields of PAN/Ag and tar/PAN/Ag electrospun nanofibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{\text{PAN}}$ (wt%)</th>
<th>$C_{\text{Tar}}$ (wt%)</th>
<th>RSP</th>
<th>Carbon Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN/Ag</td>
<td>10</td>
<td>0</td>
<td>1/10</td>
<td>45</td>
</tr>
<tr>
<td>50Tar/PAN/Ag</td>
<td>10</td>
<td>50</td>
<td>1/10</td>
<td>44</td>
</tr>
<tr>
<td>100Tar/PAN/Ag</td>
<td>10</td>
<td>100</td>
<td>1/10</td>
<td>42</td>
</tr>
</tbody>
</table>

$C_{\text{PAN}}$ is the concentration of PAN in the suspensions; $C_{\text{Tar}}$ is the content of tar based on the weight of PAN; RSP is the molar ratio of silver nitrate to the repeating unit of PAN; Carbon yield is based by the weight ratio of carbonized nanofibers and as-spun nanofibers.

Subsequently, each precursor suspension was loaded into a 5 mL BD plastic syringe attached with a stainless steel needle tip (internal diameter 0.584 mm). The needle was connected
to a high-voltage power supply (Gamma High Voltage Research, Ormond Beach, FL, USA), which generated a positive DC voltage of 15 kV. The flow rate of the suspensions was controlled at 0.5 mL/h by an electric syringe pump (Chemyx Fusion 100, Stafford, TX, USA). A grounded metal plate covered with aluminum foil served as the collector, which was horizontally placed and perpendicular to the needle tip with a 20 cm separation. The collected nanofibers were dried in a vacuum oven to remove the residual solvent and stored in a desiccator prior to further treatments. The as-spun nanofibers were designated as PAN/Ag, 50Tar/PAN/Ag, and 100Tar/PAN/Ag with tar contents of 0, 50, and 100 wt% based on PAN by weight, respectively.

4.2.3 Stabilization and Carbonization

The following stabilization and carbonization were performed in a high temperature tubular furnace (GSL-1100, MTI Corporation, Richmond, CA, USA). The as-spun nanofibers were stabilized in air by heating up to 300 °C at a heating rate of 1 °C/min and holding at this temperature for 1 h. The stabilized nanofibers were subsequently carbonized in N$_2$ atmosphere by heating up to 900 °C at a heating rate of 5 °C/min and holding at this temperature for 1 h. The resultant CNFs are designated as PAN/Ag-CN F, 50Tar/PAN/Ag-CN F, and 100Tar/PAN/Ag-CN F, respectively.

4.2.4 Characterizations

Shear viscosities of the precursor suspensions were measured using a rheometer with a 40 mm cone-plate geometry (AR2000ex, TA Instruments, New Castle, DE, USA). The apparent viscosities were recorded at shear rates ranging from 0.1 to 1000 s$^{-1}$ for each suspension at a controlled temperature of 25 °C using a Peltier device. A solvent trap cover was used to avoid solvent evaporation during the measurements. UV-vis measurements were performed to confirm Ag nanoparticle formation with a Varian UV-vis spectrophotometer (Evolution 600, Thermo
Electron Corp., USA). The UV absorbance was collected at a wavelength range of 300-600 cm\(^{-1}\) for the electrospun suspensions diluted with the solvent (DMF).

Surface morphologies of the as-spun nanofibers and CNFs were examined by a field emission scanning electron microscope (FE-SEM, FEI QuantaTM 3D FEG Dual Beam SEM/FIB, Hillsboro, OR, USA) operated at 10 kV. The as-spun nanofibers were coated with a thin layer of gold prior to FE-SEM observation and the CNFs were observed without coating. The diameters of the as-spun nanofibers and CNFs were obtained by measuring the randomly selected nanofibers on the FE-SEM images using an image processing software (Image J 1.48). Fifty individual nanofibers were measured for each sample to determine the average diameter. The chemical structure information of the as-spun, stabilized, and carbonized nanofibers was obtained from a Bruker FTIR spectrometer (Alpha, Bruker Optics Inc., Billerica, MA, USA) with an attenuated total reflectance (ATR) mode. The spectra were recorded between 4000 and 600 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\).

Thermal degradation of the as-spun and stabilized nanofibers was studied with a TA Q50 analyzer (New Castle, DE, USA) at a resolution of 0.1 μg. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were collected from 30 to 600 °C for the as-spun nanofibers and from 30 to 800 °C for the stabilized nanofibers at a heating rate of 10 °C/min. Sample weight was about 5.0 mg and the test was conducted in a N\(_2\) atmosphere with a N\(_2\) flow rate of 60 mL/min. Differential scanning calorimetry (DSC) measurements were performed with a TA Q200 system in a nitrogen atmosphere. Each sample with an approximate weight of 5 mg was scanned from 40 to 350 °C at a heating rate of 10 °C/min.

N\(_2\) adsorption and desorption isotherms of the as-spun and CNFs were measured at 77 K on a Micromeritics TriStar II 3020 analyzer (Norcross, GA, United States). The samples were
outgassed at 110 °C for 24 h prior to data collection. The specific surface area and pore size distribution of the as-spun nanofibers were calculated using the Braunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method. The specific surface area of the CNFs was calculated both by BET and Langmuir methods. The density function theory (DFT) assuming slit-shaped pores was used to determine the pore size distribution of the CNFs. The total pore volumes of the as-spun nanofibers and CNFs were obtained from the nitrogen adsorbed at a relative pressure of 0.99.

4.2.5 Antimicrobial Test

Antimicrobial activities of the as-spun nanofibers and CNFs against both Gram-positive *Staphylococcus aureus* (*S. aureus*) and Gram-negative *Escherichia coli* (*E. coli*) bacteria were tested according to the modified Kirby-Bauer method (Kong and Jang, 2008; Rujitanaroj et al., 2010). *S. aureus* and *E. coli* were cultivated in sterilized tryptic soy broth and incubated overnight at 37 °C in a shaking incubator. After 24 h, different dilutions were made by successively adding 1 mL aliquot of culture into 9 mL broth solution. In the same manner, five serial dilutions were made. The diluted culture of 0.2 mL was then uniformly spread on an agar plate. The as-spun nanofiber and CNF membranes were cut into rectangles of 10 × 5 mm², sterilized by UV irradiation for 30 min, and placed on the agar plates containing bacteria for cultivation in an incubator at 37 °C for 24 h. Finally, the inhibition zones were observed after 24 h to assess the antimicrobial capability of the as-spun nanofibers and CNFs.

4.3 RESULTS AND DISCUSSION

4.3.1 Properties of electrospinning suspensions

A homogeneous precursor suspension is a key prerequisite for successfully producing smooth and continuous electrospun nanofiber. In this study, homogeneous suspensions
consisting of biomass tar, PAN, and silver nanoparticles were obtained using DMF as solvent, due to its outstanding solubilization power for PAN and good dispersing ability for biomass tar. The shear viscosities of the precursor suspensions at a shear rate range of 0.1-1000 s⁻¹ are shown in Figure 4.1A. The suspension without tar (PAN/Ag) exhibited Newtonian fluid behavior without obvious viscosity variations at low shear rates. Then, the viscosity decreased at high shear rates and a pseudoplastic behavior was observed, due to gradual disentanglements of PAN chains by an increased shear stress. The suspension of 50Tar/PAN/Ag showed a similar behavior, but its viscosity value decreased nearly by half compared to the suspension of PAN/Ag, as a result of the disruption of PAN molecular chain-chain interactions by the tar. The 100Tar/PAN/Ag showed almost the same viscosities as the 50Tar/PAN/Ag at middle and high shear rates, but exhibited higher viscosities at low shear rates. The initial shear thinning behavior at low shear rates was caused by the higher concentration of tar in the 100Tar/PAN/Ag. The disruption of chain entanglements by an increasing tar content made PAN molecules much easier to align, leading to the immediate pseudoplastic fluid behavior at low shear rates.

Figure 4.1 Basic properties of the electrospinning suspensions. (A) The shear viscosity-shear rate relationships for PAN/Ag, 50 Tar/PAN/Ag, and 100Tar/PAN/Ag; (B) UV absorbance of PAN and PAN/Ag.

AgNO₃ was dissolved at a low temperature and then reduced to silver nanoparticles by direct heating. DMF and the polyphenols in the tar probably served as reducing agents
This green method was applied to avoid the use of environmentally hazardous chemical reducing agents such as NaBH$_4$ and dimethylhydrazine. To confirm the formation of silver nanoparticles, UV absorbance of the suspensions was measured (Figure 4.1B). The PAN/Ag suspension showed an intensive absorbance peak at about 420 nm, while no peak around this wavelength was observed for pure PAN solution. This peak was the characteristic surface plasmon resonance (SPR) band of silver nanoparticles (Abdelgawad et al., 2014; Li et al., 2015), and its presence indicated the formation of silver nanoparticles by reducing AgNO$_3$ in the suspensions.

4.3.2 Surface Morphology

Continuous electrospun nanofibers without beads were produced from the precursor suspensions with different tar/PAN ratios (Figure 4.2). However, some bulges appeared and became more obvious with increased tar content in the as-spun nanofibers, especially for the 100Tar/PAN/Ag composition. The rough surface resulted from aggregations of tar at a higher concentration and phase separations between the tar and PAN when the solvent rapidly evaporated during the travelling of electrospinning jets toward the collector (Park et al., 2004). Further increase in the tar loading levels made the electrospinning much more difficult and impractical, due to undesirable tar aggregations and formations of inhomogeneous electrospinning suspensions. The average diameter of the as-spun nanofibers increased with an increase of tar content, with the values of (392±48) nm, (613±50) nm, and (903±137) nm for PAN/Ag, 50Tar/PAN/Ag, and 100Tar/PAN/Ag, respectively (Figure 4.3). The increasing trend of the average diameters of the as-spun nanofibers with increased tar contents was due to increased concentrations of solutes (tar and PAN) in the precursor suspensions and lower contents of the solvent (DMF). In addition, the diameter variations of the as-spun nanofibers
became much larger (Figure 4.3), resulting from rougher surfaces and more non-uniformly sized nanofibers with increased tar addition.

![FE-SEM micrographs of the as-spun nanofibers and CNFs](image)

Figure 4.2 FE-SEM micrographs of the as-spun nanofibers (A: PAN/Ag, C: 50Tar/PAN/Ag, E: 100Tar/PAN/Ag) and CNFs (B: PAN/Ag-CNF, D: 50Tar/PAN/Ag-CNF, F: 100Tar/PAN/Ag-CNF) (The inset at the bottom-right of each micrograph shows a higher magnification image)

After the as-spun nanofibers were converted to CNFs by the stabilization and carbonization, the continuous fibrous morphology was preserved (Figure 4.2). Compared with as-spun nanofibers, the average diameters of the CNFs decreased to (226±21) nm, (359±34) nm, and (507±71) nm for PAN/Ag-CNF, 50Tar/PAN/Ag-CNF, and 100Tar/PAN/Ag-CNF, respectively (Figure 4.3). The resultant CNFs became more uniformly sized with smaller diameter variations,
compared to the as-spun nanofibers. This was caused by thermal decompositions and shrinkages of the as-spun nanofibers in the stabilization and carbonization processes. The thermal decompositions (mainly of tar components) also created more pores on surfaces of the CNFs, especially for the 100Tar/PAN/Ag-CNF (inset of Figure 4.2F).

Figure 4.3 A comparison of average diameters of the as-spun nanofibers and CNFs from three different formulations

4.3.3 Chemical Structure

ATR-FTIR spectra of the as-spun nanofibers are shown in Figure 4.4A. The distinctive absorbance features for PAN were present in all the as-spun nanofibers, including C≡N stretching at 2245 cm\(^{-1}\), CH\(_2\) bending at 1452 cm\(^{-1}\), CH wagging at 1256 cm\(^{-1}\), and skeletal vibration of PAN molecular chain at 1072 cm\(^{-1}\) (Arshad et al., 2011; Kampalanonwat and Supaphol, 2010; Liang and Krimm, 1958). Compared with PAN/Ag, the 50Tar/PAN/Ag and 100Tar/PAN/Ag compositions exhibited additional absorption peaks attributed to the main tar components (i.e., phenols, aromatics, acids, etc), including 3300-3400 cm\(^{-1}\) (OH stretching), 1705 cm\(^{-1}\) (carbonyl stretching), 1609 cm\(^{-1}\) (aromatic skeletal vibration), 830 cm\(^{-1}\) and 764 cm\(^{-1}\) (C-H out-of-plane bending of aromatics) (Park et al., 2004; Song et al., 2015a). These absorption peaks were not found in the PAN/Ag without tar, indicating that the tar was successfully
incorporated in the tar containing as-spun nanofibers. In addition, the peaks at 2933 and 2871 cm\(^{-1}\) were ascribed to CH\(_2\) stretching of both PAN and tar.

![ATR-FTIR spectra](image)

Figure 4.4 ATR-FTIR spectra of the as-spun (A), stabilized (B), and carbonized (C) nanofibers for different tar loading levels (I-PAN/Ag, II-50Tar/PAN/Ag, and III-100Tar/PAN/Ag)

The chemical structure of the as-spun nanofibers was significantly altered by the oxidative stabilization treatment (Figure 4.4B). The most significant change was the decrease in the intensity of C≡N absorption at 2245 cm\(^{-1}\) for all the stabilized nanofibers. In addition, new absorption peaks at 1584 cm\(^{-1}\) attributed to the combination of C=N and C=C stretching, 1340 cm\(^{-1}\) ascribed to O-H bending (in-plane), and 806 cm\(^{-1}\) due to C=C-H bending were present (Dalton et al., 1999; Wu and Qin, 2014; Zhang et al., 2003). These absorption peaks resulted from the generations of conjugated C=N containing structures from intramolecular cyclization of the nitrile groups, and conjugated C=C structures from dehydrogenations at the stabilization
stage (Frank et al., 2014; Wu and Qin, 2014). In addition, the broad absorption band at 3100-3500 cm⁻¹ was attributed to the overlaps of the stretching bands from aromatic C-H, O-H, and N-H stretching in the stabilized nanofibers. Previous researches also reported carbonyl groups at 1680 cm⁻¹ (Dalton et al., 1999; Zhang et al., 2003), but this was not obvious in the present study. These oxygen-containing groups (i.e., hydroxyl and carbonyl) were induced by the oxidative stabilization processes. The stabilized nanofibers were then subjected to thermal treatment in an inert atmosphere and thereby converted into the CNFs. Volatile compounds (e.g., HCN, H₂O, N₂, etc.) were removed to give the CNFs with a high carbon yield with respect to the original as-spun nanofibers. The FTIR spectra of the CNFs showed little discernible structure due to strong absorbance of carbon (Figure 4.4C).

### 4.3.4 Thermal Properties

![Figure 4.5 TG and DTG curves of the as-spun (A) and stabilized (B) nanofibers with three different tar contents](image)

Thermal stability of the as-spun and stabilized nanofibers is shown in Figure 4.5. The PAN/Ag as-spun nanofibers, with no obvious weight loss up to 300 °C, underwent a fast decomposition stage from 300 to 350 °C (Figure 4.5A). However, the 50Tar/PAN/Ag and 100Tar/PAN/Ag as-spun nanofibers began to degrade at a much lower temperature than the PAN/Ag nanofibers, due to lower initial degradation temperatures of tar components (Song et al.,
This was consistent with the DTG peaks of the as-spun nanofibers, which moved toward lower temperatures with increased tar contents. The residual weights of the PAN/Ag, 50Tar/PAN/Ag, and 100Tar/PAN/Ag as-spun nanofibers at 600 °C were 63%, 58%, and 49%, respectively. The main decomposition temperatures of the stabilized nanofibers shifted to higher temperatures compared to the corresponding as-spun nanofibers, indicating the effectiveness of thermo-oxidative stabilization treatments. The main weight loss of stabilized nanofibers was mainly due to the removing of volatile compounds by crosslinking condensation, dehydrogenation, and denitrogenation reactions (Frank et al., 2014). In addition, the DTG peaks of the stabilized nanofibers at approximately 180 °C were attributed to decompositions of the oxygen-containing groups, such as C=O and OH, in the stabilized nanofibers. Because of these thermal degradations, the precursor nanofibers shrunk and the formed CNFs exhibited reduced and more uniform diameters, confirming the morphological observations.

Figure 4.6 DSC curves of the as-spun (A) and stabilized (B) nanofibers with different tar contents

DSC curves of the as-spun PAN/Ag nanofibers showed a sharp exothermic peak at 317 °C (Figure 4.6A), attributed to the cyclization reactions of the nitrile groups in PAN (Frank et al., 2014; Kim et al., 1993; Zhang et al., 2003). Through the cyclization, the PAN polymer chains were converted into a heteroaromatic ladder structure. After the tar additions, the as-spun
nanofibers exhibited a broader peak and initiated the cyclization reactions at lower temperatures. The peak temperature of the 100Tar/PAN/Ag (305 °C) was much lower than that of the PAN/Ag (317 °C), although there was no obvious difference between the PAN/Ag and 50Tar/PAN/Ag (319 °C). These changes with tar additions indicated the change of the cyclization mechanism of PAN. It was recognized that the cyclization of PAN homopolymer initiated by a radical mechanism was faster than the cyclization of PAN copolymers following an ionic mechanism (Frank et al., 2014; Gupta et al., 1991). The ionizable groups of tar, such as hydroxyl and carboxylic groups located at the interfaces of PAN and tar, initiated catalytically the cyclization reactions of PAN and lowered the onset temperatures (Kim et al., 1993). Although the tar slowed down cyclization reactions of PAN to avoid fusion of the as-spun nanofibers due to overheating by sharply exothermic reactions at subsequent thermal stabilization and carbonization, some structural flaws could be induced in resultant CNFs by these ionic groups of tar, leading to inferior mechanical properties (Zhang et al., 2003). When the as-spun nanofibers were stabilized in air, the introduced oxygen-containing groups helped improve the hygroscopicity of the stabilized nanofibers (Wu and Qin, 2014; Zhang et al., 2003). Thus, the endotherm peaks at 90-110 °C of the stabilized nanofibers were due to the release of water (Figure 4.6B). In addition, the PAN cyclization peaks of the stabilized nanofibers became hardly seen, indicating basic completions of the oxidative stabilization.

4.3.5 Pore Structure

N₂ adsorption/desorption isotherms and pore size distributions of the as-spun and CNFs are shown in Figure 4.7. According to the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al., 1985), the isotherms of the as-spun nanofibers were type IV with a H3 type hysteresis loop (Figure 4.7A), indicating the presence of mesopores (2 nm<pore
size <50 nm) in the nanofibers with a non-uniform size. This was consistent with the wide pore size distributions of the electrospun nanofibers determined by the BJH method (Figure 4.7C), with peak values of 3.5, 11.4, and 18.6 nm for the PAN/Ag, 50Tar/PAN/Ag, and 100Tar/PAN/Ag, respectively. The BET specific surface area and total pore volume of the as-spun nanofibers also increased with an increase of tar loading levels (Table 4.2). The increase in specific surface area, pore volume, and pore size with increased tar content in the as-spun nanofibers was attributed to phase separations of tar and PAN. The complex composition of tar made it extremely difficult to be well blended with PAN. Thus, phase separations between the tar and PAN during solvent evaporation contributed to the increase of surface area, volume, and size of pores. This became more obvious when the tar components aggregated in some domains of the as-spun nanofibers.

Figure 4.7 N₂ adsorption/desorption isotherms and pore size distribution of the as-spun nanofibers (A and C) and CNFs (B and D) with different tar contents
During the stabilization and carbonization processes of the as-spun nanofibers, their pore structure underwent dramatic changes. Compared to the as-spun nanofibers, the CNFs had much higher specific surface areas and pore volumes (Table 4.2). Based on the IUPAC classification (Sing et al., 1985), the isotherms of the CNFs are typical of type I (Figure 4.7B), indicating the dominance of micropores, which is similar to other PAN based carbon fibers (Park and Jang, 2003). The N$_2$ adsorption completed at very low relative pressure regions (P/Po<0.05) because of multidirectional interactions between pore walls and the adsorbate. The pore size distribution calculated by DFT showed that the CNFs had a uniform pore size with peak values of 1.7, 1.6, and 1.7 nm for PAN/Ag-CN$_2$, 50Tar/PAN/Ag-CN$_2$, and 100Tar/PAN/Ag-CN$_2$, respectively, confirming the predominance of micropores (Figure 4.7D). The tar-containing CNFs showed a much larger N$_2$ adsorption capacity as compared to that of the CNFs without tar (Figure 4.7B). The specific surface area of the CNFs calculated by both BET and Langmuir methods indicated a large increase when the tar was added, and the pore volumes exhibited the same trend (Table 4.2), consistent with the FE-SEM observation. Furthermore, the fraction of micropore volumes for 50Tar/PAN/Ag-CN$_2$ (99.1%) and 100Tar/PAN/Ag-CN$_2$ (97%) was much higher than that for PAN/Ag-CN$_2$ (74.2%), similar to the results of pitch based electrospun carbon fibers (Park et al., 2003). The large increase in the specific surface area and the high microporosity obtained with the tar incorporation was attributed to the combined effects of the phase separations between the tar and PAN, and thermal decompositions of the tar constituents. A similar result was reported for the PAN/pitch derived electrospun CNFs (Kim et al., 2011). The noticeably different structures of the tar and PAN caused inhomogeneous distributions of the tar in the PAN matrix and formation of tar aggregates throughout the as-spun nanofibers. Some aggregates of the tar degraded thermally when the as-spun nanofibers were converted to the CNFs. Thus, more pores
(mainly micropores) were created with tar addition, leading to increased specific surface areas and larger micropore volumes in the CNFs (Figure 4.8).

Table 4.2 Specific surface area and pore volumes of the as-spun nanofibers and CNFs

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$S_{\text{Langmuir}}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{mp}$ (cm$^3$/g)</th>
<th>$V_{mp}/V_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN/Ag</td>
<td>6.54</td>
<td>0.013</td>
<td>0.0009</td>
<td>6.9</td>
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<tr>
<td>50Tar/PAN/Ag</td>
<td>8.29</td>
<td>0.033</td>
<td>0.0006</td>
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<td></td>
</tr>
<tr>
<td>100Tar/PAN/Ag</td>
<td>8.24</td>
<td>0.032</td>
<td>0.0005</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>PAN/Ag-CNf</td>
<td>94.79</td>
<td>97.78</td>
<td>0.043</td>
<td>74.2</td>
<td></td>
</tr>
<tr>
<td>50Tar/PAN/Ag-CNf</td>
<td>410.25</td>
<td>414.38</td>
<td>0.133</td>
<td>99.1</td>
<td></td>
</tr>
<tr>
<td>100Tar/PAN/Ag-CNf</td>
<td>437.81</td>
<td>439.50</td>
<td>0.144</td>
<td>97.0</td>
<td></td>
</tr>
</tbody>
</table>

$S_{\text{BET}}$ is BET specific surface area; $S_{\text{Langmuir}}$ is the specific surface area calculated by Langmuir model; $V_p$ is the total pore volume; $V_{mp}$ is the micropore volume; $V_{mp}/V_p$ is the fraction of micropore volume.

Figure 4.8 A schematic illustrating the fabrication of the porous tar-derived CNFs through electrospinning followed by stabilization and carbonization processes
4.3.6 Antimicrobial Performance

Figure 4.9 Antimicrobial activities of the as-spun nanofibers (upper row) and CNFs (lower row) with different tar contents against \textit{S. aureus}

Formation of inhibition zones around the as-spun nanofibers and CNFs were monitored in order to evaluate their antimicrobial activities against \textit{S. aureus} (Figure 4.9). The similar situation was observed for \textit{E. coli} (the figure is not shown). Clear inhibition zones around the as-spun nanofiber samples were observed after 24 h incubation, indicating their excellent antimicrobial efficiency against both \textit{S. aureus} and \textit{E. coli}. The antimicrobial activities were preserved after the stabilization and carbonization processes, with obvious formation of inhibition zones around the CNFs. Silver nanoparticles with their effective biocidal ability were incorporated into the nanofibers to give antimicrobial capabilities, although the mechanism of killing microorganisms by silver was not clearly explained (Kong and Jang, 2008; Li et al., 1998; Song et al., 2011). In this study, the silver nanoparticles were proposed to diffuse into the broth and to inhibit the growth of bacteria. The porous features of the as-spun nanofibers and CNFs resulted in large specific surface areas and pore volumes, which made the diffusion of silver nanoparticles into the broth more easily, increasing the exposure and contact of silver nanoparticles to the bacteria (Figure 4.8) (Kong and Jang, 2008). Consequently, the tar
containing as-spun nanofibers and CNFs had higher specific surface areas and pore volumes, which might enhance their antimicrobial efficacy. The effect of tar loading levels on the antimicrobial performance of as-spun nanofibers and CNFs needs to be further studied. The antimicrobial efficacy was affected by the porosity and pore size distribution of the carbon materials which could be controlled by tuning the composition and concentration of tar. Electrospun polymer nanofibers incorporated with silver nanoparticles were intensively studied and showed attractive applications in wound dressing, tissue scaffolds, and package materials (Rujitanaroj et al., 2008; Xing et al., 2010). The incorporation of tar could reduce the cost of silver-based antimicrobial materials.

4.4 CONCLUSIONS

Continuous microporous CNFs from biomass tar/PAN/silver hybrids with antimicrobial capabilities were fabricated through electrospinning and subsequent thermal stabilization and carbonization. Silver nitrate was reduced to silver nanoparticles, which conferred the antimicrobial abilities to the as-spun nanofibers and CNFs. The as-spun nanofibers showed larger average diameters with increased tar loading levels, due to larger concentrations of tar and PAN in the suspensions. However, the increased contents of tar made the fiber surface rougher and increased fiber diameter variations resulted from tar aggregations and phase separations between tar and PAN. In addition, the incorporation of tar reduced the thermal stability of the as-spun nanofibers due to relatively lower onset degradation temperatures of the tar components. The tar also slowed down the cyclization reactions of PAN by its ionizable groups, which was helpful for subsequent stabilization processes. The as-spun nanofibers exhibited mesopore characteristics while micropores dominated in the CNFs due to the combined effects of thermal decompositions of some tar constituents and phase separations of tar and PAN. The large
specific surface areas and the volumes of pores of the as-spun nanofibers and CNFs made the silver nanoparticles more easily diffuse into the broth, endowing their excellent antimicrobial abilities. Therefore, biomass tar can be a low-cost precursor for manufacturing antimicrobial carbon materials, extending applications of biomass products and reducing environmental pollutions associated to tar disposal.

4.5 REFERENCES


CHAPTER 5 RHEOLOGICAL AND FLUID FILTRATION PROPERTIES OF LOW SOLID DRILLING FLUIDS ADDED WITH CELLULOSE NANOPARTICLES

5.1 INTRODUCTION

In oil and gas industry, bentonite is a montomorillonite clay commonly used in drilling fluids due to its inherent and well-performing rheological properties (Baruah et al., 2013; Bourgoyne et al., 1991; Hermoso et al., 2015). The bentonite suspensions exhibit excellent shear thinning behavior that offers a good pumpability of drilling fluids and outstanding carrying capacity of drilled cuttings (Bourgoyne et al., 1991). The viscosity of bentonite-based drilling fluids is accomplished by arranging bentonite particles into an edge-to-face orientation (Luckham and Rossi, 1999). In conventional drilling fluids, a relatively large content of bentonite is needed to achieve the anticipated rheological and filtration characteristics. However, a high concentration of bentonite in drilling fluids can lower drilling efficiency and even result in a series of problems such as differential sticking, inefficient wellbore cleaning, and formation damage. Consequently, a properly designed low-solid system that has a lower solid content than conventional bentonite drilling fluids is desired for faster penetration rates, thinner filter cakes, highly efficient wellbore cleaning, easier fluid maintenance, and improved hydraulics. Low solid drilling fluids can be prepared by substituting one or more polymers for bentonite, which gives rheology and fluid loss properties comparable to that of a higher concentration of ordinary bentonite. A wide range of polymeric additives, including xanthan gum, starch, sodium carboxymethyl cellulose, polyanionic cellulose, polyacrylamide, and polyacrylate, can be added into drilling fluids for achieving desired rheological and filtration properties (Fereydouni et al., 2012; Hamed and Belhadri, 2009; Jang et al., 2015; Menezes et al., 2010).

Recently, micro and nanoparticles are attracting more attention for improving the performance of drilling fluids to meet increasing challenges in drilling and production of oil and
gas from non-conventional reservoirs and under harsh conditions such as high temperature and high pressure (Abdo and Haneef, 2012; Al-Yasiri and Al-Sallami, 2015). Such micro and nanoparticles play an essential role in decreasing the permeability of shale formation, maintaining borehole stability, intensifying mud cake quality, reducing fluid loss, improving cutting removal ability, lowering the friction, eliminating differential pipe sticking, protecting reservoir, and enhancing oil and gas recovery (Kasiralvalad, 2014). To achieve these goals, a variety of micro and nanoparticles have been studied, including nano-silica (Sensoy et al., 2009; Sharma et al., 2012), nano metallic oxide (Barry et al., 2015; Cheraghian et al., 2013; Sayyadnejad et al., 2008), graphite and grapheme oxide (Kosynkin et al., 2011; Nasser et al., 2013), clay nanoparticles (Abdo and Haneef, 2013), polymer-based nanoparticles (Jiang et al., 2009; Qu et al., 2007), and combinations of these nanoparticles. Drilling technologists can modify rheological and fluid filtration properties of the drilling fluids by changing type, composition, size distribution, surface characteristics of the nanoparticles to meet requirements of any particular situation of drilling and production. In most cases, a very low concentration (<1%) of nanoparticles is needed in these nano-enhanced drilling fluids (Amanullah et al., 2011). Thus, nanoparticles can be good potential candidates for formulating low solid drilling fluids. However, most of the above nanoparticles are non-renewable and non-biodegradable and their use subjects to cost and environmental impact. Therefore, it is highly desirable to develop renewable, biodegradable, and more cost-effective nanoparticle additives in low solid drilling fluids.

Cellulose is the most abundant renewable and biodegradable biopolymer in nature, which widely exists in various natural resources, such as wood, cotton, hemp, linen, chitin, and bacteria (Moon et al., 2011). Cellulose nanoparticles (CNPs), including cellulose nanocrystals (CNCs)
and cellulose nanofibers (CNFs), can be obtained from these cellulosic source materials by a purification pretreatment followed by chemical or mechanical separation approaches, including acid hydrolysis, enzyme hydrolysis, 2,2,6,6-Tetramethyl-1-piperidyloxy (TEMPO) mediated oxidation, ultrasonic, grinding, and high-pressure homogenization treatments (Chun et al., 2011; Moon et al., 2011). CNPs have a high specific surface area, large aspect ratio, and high thermal stability (Cho and Park, 2011; Li et al., 2015a). In addition, aqueous suspensions of CNPs exhibit similar fluid flow properties to those of bentonite, with low viscosities at high flow rates and high viscosities at low flow rates (Li et al., 2015b). These excellent characteristics attracted the interest to use CNPs as efficient additives for producing technically reliable, economically attractive, environmentally friendly low solid drilling fluids to meet the technical needs and challenges of the oil and gas industry.

The objective of this study was to develop novel and eco-friendly low solid drilling fluids formulated with bentonite, polyanionic cellulose (PAC), and CNPs, including CNCs and CNFs. The effects of concentrations and morphology of CNPs on the rheological and fluid filtration properties of the low solid drilling fluids were investigated. The changes of filter cake characteristics including surface morphologies, thickness, porosity, and permeability in response to additions of the CNPs in the fluid systems were studied to in-depth understand the interactions between CNPs and bentonite.

5.2 MATERIALS AND METHODS

5.2.1 Materials

Wyoming sodium bentonite was supplied from Baroid Industrial Drilling Products Inc. (Houston, TX, USA). PAC was used as a filtration control agent and purchased from Halliburton Company (Houston, TX, USA). Sulfuric acid was applied from Sigma-Aldrich (St. Louis, MO,
USA). CNFs (Celish KY 100-S Grade) were purchased from Daicel Chemical Industries, Ltd. (Tokyo, Japan). CNCs were produced through the hydrolysis of CNFs using 64% sulfuric acid at 45°C for 1 h and further mechanical separation processes by a high-pressure homogenizer (Microfluidizer M-110P, Microfluidics Corp., Newton, MA, USA). The morphologies of CNFs and CNCs were examined by a transmission electron microscope (TEM, JEOL 100 CX, JEOL USA Inc., Peabody, MA, USA), with an accelerating voltage at 80 kV. The width distribution of CNFs and CNCs was obtained from the analysis of TEM images using an image processing software (ImageJ 1.48). Fifty individual fibers were randomly selected to measure the width and length of each.

### 5.2.2 Formulations of Drilling Fluids

| Table 5.1 Formulations of the bentonite drilling fluids added with CNPs |
|----------------|-----------------|-----------------|-----------------|-----------------|
|                | Bentonite (g)   | CNPs (g)        | PAC (g)         | Water (mL)     |
| BT6            | 21.0            | 0               | 0.3             | 328.7          |
| BT6/CNP0.05    | 21.0            | 0.175           | 0.3             | 328.5          |
| BT5/CNP0.10    | 17.5            | 0.350           | 0.3             | 331.9          |
| BT4/CNP0.15    | 14.0            | 0.525           | 0.3             | 335.2          |
| BT3/CNP0.20    | 10.5            | 0.700           | 0.3             | 338.5          |
| BT2/CNP0.25    | 7.0             | 0.875           | 0.3             | 341.8          |
| BT1/CNP0.30    | 3.5             | 1.050           | 0.3             | 345.2          |
| CNP0.40        | 0               | 1.400           | 0.3             | 348.3          |

The bentonite, bentonite/CNPs, and CNP suspensions were prepared in a standard 350 mL laboratory barrel (Table 5.1). Specifically, CNFs and CNCs were dispersed in water under vigorous mechanical stirring for 30 min at room temperature. The bentonite powder was then added and stirred for 10 min. Finally, PAC was added into the above suspensions and stirred for
another 10 min. The nomenclature of the drilling fluids samples is designated as BTx, BTx/CNPy, and CNPy, where x (wt%) and y (wt%) are the concentrations of bentonite and CNPs (i.e., CNFs or CNCs) based on the final weight of drilling fluids.

5.2.3 Rheological Testing

Rheological properties of the drilling fluids were tested by two types of viscometers. A sophisticated TA rheometer equipped with a standard Peltier concentric cylinder geometry (AR2000ex, TA Instruments, New Castle, DE, USA) was used to measure the viscosities of the drilling fluids under a wide range of shear rates. Concentric cylinder geometries are commonly used for testing low viscosity fluids such as drilling fluids. The geometry includes a stainless steel cup with a radius of 15.19 mm, configured by a rotator with a radius of 14.01 mm. The apparent viscosities were measured at shear rates ranging from 0.1 to 1000 s\(^{-1}\) with a controlled temperature of 25°C using the Peltier device. A 20 mL sample of drilling fluids was tested for each measurement.

In addition, an industrial rotating viscometer (NL Baroid, NL Industries, Inc., Houston, TX) was used to measure viscosities, yield point, and gel strength of the drilling fluids according to American Petroleum Institute (API) standard. The drilling fluids were stirred before measuring to ensure that the steady-state conditions were met. The rheological parameters including apparent viscosity (\(\mu_a\)), plastic viscosity (\(\mu_p\)), and yield point (\(\tau_y\)) were obtained by the following equations:

\[
\mu_a = \frac{\theta_{600}}{2}
\]

\[
\mu_p = \theta_{600} - \theta_{300}
\]

\[
\tau_y = \theta_{300} - \mu_p
\]
where $\theta_{300}$ and $\theta_{600}$ were the dial readings at 300 and 600 rpm, respectively. The gel strength of the drilling fluids, including Gel$_{in}$ and Gel$_{10\text{min}}$, was recorded by noting the maximum dial deflection at 3 rpm after the drilling fluid remained static for 10 s and 10 min, respectively.

5.2.4 Fluid Filtration Testing

Fluid filtration properties of the drilling fluids were evaluated by a standard filter press with a regulated CO$_2$ pressurization system and standard filter papers (Fann Instrument Co., Houston, TX). All the filtration tests were conducted at the pressure of (100±5) psi ((690±35) kPa) and the temperature of 25ºC, according to American Petroleum Institute standard. The volume of filtrate was determined by the mass of the filtrate obtained from a digital balance and the average density of the filtrate. Thus, the filtrate volume versus time was obtained for each drilling fluid system. At the end of 30 min, the filter paper with filter cake was removed from the cell and the thickness of the cake was measured. When the filter cakes dried, their surface morphologies were examined by a field emission scanning electron microscope (FE-SEM, FEI QuantaTM 3D FEG Dual Beam SEM/FIB, Hillsboro, OR, USA) operated at 10 kV. The samples of dried filter cakes were coated with a thin layer of gold prior to the FE-SEM observation.

5.3 RESULTS AND DISCUSSION

5.3.1 Fluid Rheological Properties

Drilling fluids are commonly characterized as shear thinning non-Newtonian fluids, with viscosity that decreases with an increasing shear rate (Bourgoyne et al., 1991). The drilling fluids with obvious shear thinning behaviors are more easily pumped downhole and highly desired in drilling field. The shear rate dependence of viscosities of the drilling fluids is shown in Figure 5.1. The bentonite drilling fluids (BT6) without CNPs exhibited a good shear thinning behavior. With additions of CNPs (CNCs and CNFs) and simultaneous reductions of bentonite, the
pseudoplastic behavior of the drilling fluids remained. This was due to the superior shear thinning characteristics of CNP suspensions (Li et al., 2015a; Moon et al., 2011), which was confirmed by the fluids of CNC0.40 and CNF0.40 without bentonite (Figure 5.1A, B). Therefore, CNPs could be potential good additives in low solid drilling fluids in which the amount of bentonite was reduced, considering their excellent shear thinning behavior. Moreover, the viscosities of the drilling fluids showed a decreased trend with increased additions of CNPs (Figure 5.1A, B), which was in accord with the changes of apparent viscosities measured by the industrial rotation viscometer (Table 5.2). The viscosity drop with increased CNPs and decreased bentonite contents was caused by the reduced solid content, making particles in the drilling fluids much easier to align under shear stress.

Figure 5.1 Apparent viscosity and shear stress versus shear rates of the drilling fluids
The shear rate dependence of shear stress of the drilling fluids is shown in Figure 5.1C and 5.1D. Different rheological models such as Bingham plastic model, power law model, and Herschel-Bulkey model could be used to evaluate the shear stress-shear rate relationships of the non-Newtonian drilling fluids. The Herschel-Bulkey model, as a rheological model to describe non-Newtonian fluid in non-linear way, was found to be better for characterizing the non-Newtonian behavior of drilling fluids (Barry et al., 2015). Three parameters, including yield point ($\tau_o$), consistence coefficient ($K$), and flow behavior index ($n$), were obtained according to the following equation,

$$\tau = \tau_o + K \times \dot{\gamma}^n$$

(5.4)

where $\tau$ and $\dot{\gamma}$ are shear stress and shear rate, respectively. The yield point, the stress that must be applied to initiate flow, was calculated by extrapolating the curve of shear stress against shear rate to zero-shear condition. The consistence coefficient and flow behavior index were obtained by fitting the shear stress-shear rate curve to the above equation with the 95% confidence bounds. The values of flow index were lower than 1 (Table 5.2), confirming the shear-thinning behavior of the drilling fluids. The yield point decreased with an increasing CNP content, indicating that lower force was required to start the flow of the drilling fluids but the capacity of cutting carrying might be compromised. The values of yield point measured by the industrial rotation viscometer showed a similar trend (Table 5.2). In addition, the plastic viscosities and gel strength of the drilling fluids also showed similar changes to the yield point. A decreased plastic viscosities with increased CNPs were due to the reduced low solid contents in the drilling fluids, which could improve drilling efficiency because of the low viscosity of drilling fluids at the bit. However, the lower gel strength could affect the ability of the drilling fluids to suspend drilled cuttings and weighting material when circulation was ceased. As a result, a part of bentonite
could be replaced by CNPs for producing low solid drilling fluids, but it was not practicable to apply drilling fluids with a very low content (<3 wt%).

Table 5.2 Rheological properties of the bentonite drilling fluids added with CNPs

<table>
<thead>
<tr>
<th>Formulations</th>
<th>( \mu_a ) (cP)</th>
<th>( \mu_p ) (cP)</th>
<th>( \tau_y ) (lb/100 sq ft)</th>
<th>Gel Strength (lb/100 sq ft)</th>
<th>Herschel-Bulkley Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_o ) (Pa)</td>
<td>( K ) (Pa·s)</td>
<td>( n )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT6</td>
<td>41</td>
<td>28</td>
<td>26</td>
<td>8</td>
<td>26</td>
</tr>
<tr>
<td>BT6/CNC0.05</td>
<td>46</td>
<td>29</td>
<td>29</td>
<td>11</td>
<td>33</td>
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<tr>
<td>BT5/CNC0.10</td>
<td>33</td>
<td>21</td>
<td>23</td>
<td>7</td>
<td>21</td>
</tr>
<tr>
<td>BT4/CNC0.15</td>
<td>26</td>
<td>17</td>
<td>17</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>BT3/CNC0.20</td>
<td>19</td>
<td>13</td>
<td>12</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>BT2/CNC0.25</td>
<td>14</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>BT1/CNC0.30</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CNC0.40</td>
<td>6</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>BT6/CNF0.05</td>
<td>45</td>
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<td>9</td>
<td>29</td>
</tr>
<tr>
<td>BT5/CNF0.10</td>
<td>40</td>
<td>26</td>
<td>28</td>
<td>7</td>
<td>23</td>
</tr>
<tr>
<td>BT4/CNF0.15</td>
<td>35</td>
<td>23</td>
<td>24</td>
<td>6</td>
<td>18</td>
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<tr>
<td>BT3/CNF0.20</td>
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<tr>
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<td>BT1/CNF0.30</td>
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<td>12</td>
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</tr>
<tr>
<td>CNF0.40</td>
<td>16</td>
<td>9</td>
<td>14</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

Although both CNCs and CNFs exhibited shear thinning behavior and similar trends of viscosity, yield stress, and gel strength, differences were found between them. The shear thinning behavior decreased as the solid content of the drilling fluids added with CNCs reduced from 6.14 wt% (BT6/CNC0.05) to 1.39 wt% (BT1/CNC0.30), and showed solid content dependence at low shear rates and relatively little solid content dependence at high rates (Figure 5.1A). Compared to
CNC-DF, the shear thinning behavior of the fluids incorporated with CNFs presented less solid content dependence (Figure 5.1B). Furthermore, the values of viscosities of the drilling fluids with CNCs decreased but not much from BT6/CNC0.05 to BT3/CNC0.20, and a large drop of viscosity at low shear rates were observed by further adding CNCs and reducing bentonite contents (BT2/CNC0.25 and BT1/CNC0.30). In contrast, viscosities of the drilling fluids with CNFs still had relatively larger values at very low solid contents, compared to CNC-DF. In addition, the values of apparent viscosity, plastic viscosity, yield point, and gel strength for the CNC-DF measured by the industrial rotational viscometer were larger than those for the CNF-DF, especially at very low solid contents (0.49-2.34 wt%).

Figure 5.2 TEM images and diameter distributions of the CNCs (A) and CNFs (B)

The differences in rheological properties between CNC and CNF added low solid drilling fluids can be explained by their distinct structural characteristics. CNFs were finer cellulose fibrils manufactured by mechanical refining of wood or plant fibers, and CNCs were produced by further acid hydrolysis of CNFs. CNCs were rod-like or whisker shaped nanoparticles with an average aspect ratio of 42±13 ((6.9±2.3) nm in width and (290±31) nm in length) (Figure 5.2A), but CNFs were very long and curved fibers with a much higher aspect ratio ((11.4±4.9) nm in width and up to several micrometers in length) (Figure 5.2B). Since both of them had an
average width in nanometer range (1-100 nm), they were defined as nanoparticles. CNFs were considered as reminiscent of elementary fibrils in wood and plant cellulose biosynthesis process and contained both amorphous and crystalline regions, and CNCs were reminiscent of the crystalline regions within the elementary fibrils (Moon et al., 2011). Thus, CNCs were more rigid while CNFs were more flexible. Moreover, the sulfuric acid treatment introduced sulfate groups and made surfaces of the resulted CNCs negatively charged. It was reported that more sulfate groups were found on the surface of CNCs compared to CNFs by X-ray photoelectron spectroscopy (Li et al., 2015a). The negatively charged surfaces of CNCs promoted the formation of stabilized suspensions, in which individual CNCs were well dispersed, while the CNFs were highly intertwined. This made CNCs in the suspensions much easier to align under shear than the CNFs. Consequently, the pure CNC suspension (CNF0.40) had lower viscosities compared to CNF0.40 (Figure 5.1A, B). When CNPs and bentonite were blended in the suspensions, the differences in rheological properties of the CNC-DF and CNF-DF could be attributed to their different interactions with bentonite and CNPs. Bentonite consists of platelet layers with negatively charged surfaces (Bourgoyne et al., 1991; Luckham and Rossi, 1999). Thus, the negative charges on the surfaces of CNCs resulted in the generation of repulsive forces between CNCs and bentonite in the fluid system, which could cause their aggregations. By contrast, CNFs were produced by mechanical disintegration processes without the involvement of sulfuric acid and their surfaces were not negatively charged, so the strong aggregations were not expected in the CNFs/bentonite fluid system. Furthermore, the highly entangled CNFs could hold bentonite particles in the fluids and formed a flexible 3D network. This network increased the resistance to flow of the CNF-DF, and larger viscosities, shear stress, and gel strength than CNC-DF were observed, which became more obvious at higher CNP contents.
5.3.2 Fluid Filtration Properties

The flow of mud filtrate through a filter cake is described by the following Darcy’s Law (Bourgoyne et al., 1991).

\[
\frac{dV_f}{dt} = \frac{\kappa A \Delta p}{\mu h_c}
\]

where \(V_f\), \(t\), \(\kappa\), \(A\), \(\Delta p\), \(\mu\), \(h_c\) is the filtrate volume (mL), time (s), permeability (D), cross-section area (cm\(^2\)), pressure drop across the filter cake (atm), viscosity (cP), and thickness of filter cake (cm), respectively. The solution to Darcy’s Law can be expressed as

\[
V_f = \sqrt{\frac{2\kappa A \Delta p}{f_{sc} - 1} f_{sm}} A \sqrt{\frac{f}{\mu}}
\]

where \(f_{sc}\) is the volume fraction of solids in the drilling fluid and \(f_{sm}\) is the volume fraction of solids in the filter cake. From this equation, linear relationships between fluid filtrate loss and square root of time and linear was expected, assuming the remaining parameters were constant.
This was confirmed by the plots of filtrate volume against the square root of time for the drilling fluids added with CNPs and the control (Figure 5.3).

![Figure 5.4 Standard fluid loss and filter cake characteristics of the drilling fluids](image)

The standard water loss (30-min filtrate volume) of the drilling fluids increased slowly within the CNP concentration range of 0-0.2 wt%, but rapidly went up when the CNP concentration was larger than 0.2 wt% (Figure 5.4A). This could be explained by further investigating the characteristics of filter cakes, including cake thickness and permeability. The thickness of filter cakes showed a decreased trend with an increasing CNP concentration (Figure 5.4B). The permeability of the filter cakes was calculated based on Darcy’s Law, assuming the constant cross-section area (45 cm²), pressure difference (690 Pa), viscosity of filtrate (1×10⁻³ Pa·s), and temperature (25°C). No significant changes in the permeability of filter cakes were observed with varied CNP concentration except for CNF0.40 (Figure 5.4D). It should be pointed

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out that the filtration of CNC0.40 could not be measured successfully due to combined effects of the extremely low solid content (0.40 wt%) and small dimensions of CNCs, resulting in filtrate spurting out shortly after the pressure was applied. According to the Darcy’s Law, the fluid loss was proportional to the permeability, but inversely proportional to cake thickness. Therefore, the increased fluid loss of the drilling fluids with the increased CNP concentration was mainly due to the decreased cake thickness, especially when the CNP concentration was larger than 0.2 wt%.

Figure 5.5 FE-SEM images of filter cakes formed by the drilling fluids of BT6 (A), BT1/CNC0.30 (B), BT1/CNF0.30 (C), and CNF0.40 (D)

Although the filtrate volume of CNC-DF and CNF-DF showed the same trend with varied concentrations of CNCs or CNFs and there was no obvious difference in the standard fluid loss between them, it was found that their filter cakes had different characteristics. The filter cakes of CNC-DF exhibited lower values of thickness and permeability but higher porosity, compared to CNF-DF (Figure 5.4). The porosity was calculated by the following equation,
\[
\phi = \frac{4(W_w - W_d)}{\pi \rho D^2 h_c}
\]  

(5.7)

where \( \phi \), \( W_w \), \( W_d \), \( \rho \), \( D \) is the porosity of filter cakes, weight of wet filter cakes, weight of dried filter cakes, density of filtrate, and diameter of wet filter cake, respectively. In addition, the filter cakes of CNC-DF and CNF-DF also showed different surface microstructure observed by FE-SEM (Figure 5.5). The filter cake of CNC-DF presented no significantly different surface morphologies from that of the control, and no CNCs were discernible due to their small dimensions (Figure 5.5A, B). By contrast, the CNFs were easily observed on the surfaces of filter cake from CNF-DF and these fibers bound bentonite particles closely, like tree roots in the soil (Figure 5.5C). When no bentonite was added, the CNF network was more obvious (Figure 5.5D).

The differences in features of filter cakes between CNC-DF and CNF-DF were attributed to their different surface morphologies and interactions with bentonite. As discussed above, the electrostatic repulsive forces between CNCs and bentonite promoted their aggregation, and CNCs and bentonite dominated regions formed separately (Figure 5.6). These separations contributed to the higher porosity of filter cakes formed by CNC-DF, compared to CNF-DF (Figure 5.4C). The higher porosity of CNC-DF filter cakes did not result in larger permeability, since the pores were confined by the surrounding CNCs and bentonite particles, and these pores were not interconnected sufficiently. However, the thin and long CNFs bound the dispersed bentonite particles closely and forming a flexible 3D network, resulting in relatively low porosity of filter cakes (Figure 5.4C). The 3D network also caused thicker filter cakes as more bentonite could be retained in the CNF/bentonite filter cakes (Figure 5.4B). This was why the cake thickness of BT6/CNF0.05 added with only 0.05 wt% CNFs was significantly larger than that of BT6, and even the cake thickness of BT5/CNF0.10 and BT4/CNF0.15 was also larger although
their solid content decreased compared to the control (Figure 5.4B). Meanwhile, it must be realized that there was still some little separation or pores between the immiscible CNFs and bentonite. Consequently, the long CNFs increased the connectivity of the pores and offered paths for the filtrate to flow through the filter cakes (Figure 5.5C, Figure 5.6), resulting in larger cake permeability compared to CNCs. The CNF0.40 was an extreme case that no bentonite existed in the CNF network, and a sudden jump in the permeability of its filter cakes was present (Figure 5.4D).

Figure 5.6 A schematic illustrating the formation of filter cakes by the drilling fluids added with CNCs and CNFs on borehole walls

From the above discussions, the abundant and environmental-friendly CNPs proved to be promising nanomaterials to manufacture low solid drilling fluids. The CNPs with very low concentrations could be added in the drilling fluids to build up a suitable viscosity at relatively low solid levels and to maintain the desired viscosity throughout the drilling operation. Effective filter cakes could be formed on the wellbore walls with the CNP added low solid drilling fluids. Moreover, the nanoparticles have the potential to improve wellbore stability by plugging pores of subsurface formations such as shale, preventing drilling fluid loss into formation and subsurface fluid intrusion into the wellbore (Sensoy et al., 2009; Wilson, 2012). However, it has to be
pointed out that a minimum amount of bentonite is required to maintain an adequate yield point and form efficient filter cakes with CNPs to prevent large fluid loss. The size distributions and surfaces of CNPs can be tailored to maximize their function as a performance modifier in low solid drilling fluids. Thus, the interactions between plate pallets of bentonite and surfaces of CNPs can be controlled and optimized to improve the rheological properties and filter cakes characteristics of the low solid drilling fluids made by them. This work demonstrates a pathway for development and applications of renewable and biodegradable nanomaterials in well service fluids, which becomes especially important with increased environmental regulation.

5.4 CONCLUSIONS

The low solid drilling fluids were successfully prepared by substituting CNPs (CNCs and CNFs) for a part of bentonite in the fluid system. Both the CNC-DF and CNF-DF exhibited similar pseudoplastic behavior, due to the excellent shear thinning characteristics of CNP suspensions. Additionally, the viscosity, yield point, and gel strength of the drilling fluids decreased with additions of CNPs. In comparison, the CNC-DF fluids had lower values of viscosity, yield point, and gel strength than CNF-DF, attributed to their distinct structure characteristics and different interactions with bentonite in the fluid system. The small size and negatively charged surfaces of CNCs caused the generation of repulsive forces with bentonite, promoting the aggregation and separation of CNCs and bentonite. In contrast, these repulsive forces were not present in CNF/bentonite fluid system, and the highly entangled CNFs formed a flexible 3D network, which increased the resistance to flow under shear stress and the larger viscosity, yield point, and gel strength were observed. On the other hand, the filtrate volume of the drilling fluids increased with an increasing content of CNPs, and no significant difference in standard fluid loss was found between CNC-DF and CNF-DF. However, the filter cakes of CNC-
DF showed lower values of thickness and permeability but higher porosity, compared to CNF-DF. The high porosity and low permeability of the filter cakes from CNC-DF were attributed to isolated pores formed by the aggregation and separation of CNCs and bentonite. The flexible 3D network of CNFs bound more bentonite particles closely, resulting thicker filter cakes with lower porosities. Meanwhile, the CNFs provided the paths of filtrate flow and increased the pore connectivity in the filter cakes, contributing to its higher permeability. The rheological and fluid filtration properties of CNP added drilling fluids could be further optimized by tailoring the size distributions and surface functionality of CNPs. A new strategy is thus provided to prepare well service fluids using biopolymer nanoparticles from renewable and biodegradable resources for oil and gas exploitation.

5.5 REFERENCES


CHAPTER 6 NOVEL BIOPOLYMER WATER-BASED DRILLING FLUIDS FOR ENHANCING DRILLING PERFORMANCE

6.1 INTRODUCTION

Drilling fluids have to perform essential tasks including controlling formation pressures, minimizing formation damage, maintaining wellbore stability, suspending and carrying out cuttings, and cooling as well as lubricating drilling bit (Bourgoyne et al., 1991; González et al., 2011). Successful drilling operations are highly dependent on the selection of drilling fluids with desirable properties which are determined by their rheological and fluid filtration properties to a large extent. Lack in required performance of drilling fluids may cause severe drilling problems such as differential sticking, lost circulation, wellbore instability, and formation damage. These problems become more serious in deep drilling due to deteriorations of drilling fluid properties resulted from considerable increase in temperature and pressure (Abdo and Haneef, 2013). The flocculation of bentonite at high temperature and high pressure (HTHP) conditions is one of main factors leading to the malfunctions of drilling fluids (Abdo et al., 2014). Therefore, it is highly desirable to find various additives to compensate for bentonite deficiencies.

Recently, nanotechnology has opened the doorway to the development of a new generation of fluids defined as smart fluids in which nanoparticles are added for improved/enhanced drilling and oil recovery (Abdo and Haneef, 2013; Farbod et al., 2015; Sun et al., 2015). Due to the unique characteristics like small dimensions and high surface area to volume ratio of nanoparticles, they attracted increasing attention as additives in drilling fluids by enhancing drilling performance, including eliminating differential pipe sticking, lowering the friction, maintaining borehole stability, reducing fluid loss, improving cutting removal ability, intensifying mud cake quality, decreasing the permeability of shale formation, reducing formation damage, and enhancing oil and gas recovery (Kasiralvalad, 2014). In order to obtain
these performance improvements, various nano additives in drilling fluids were studied. Graphene oxide presented good performance as a filtration additive in water-based drilling fluids at a very low concentration (0.2 wt%), giving an average API fluid loss of 6.1 mL and a filter cake of 20 μm thick compared to an fluid loss of 7.2 mL and a filter cake of 290 μm thick from a standard fluid in the oil industry (Kosynkin et al., 2011). Carbon nanotubes were dispersed in drilling fluids to enhance the thermal conductivity and filtration properties (Fazelabdolabadi et al., 2015). A core-shell structured nano silica composite was prepared and added into drilling fluids, which showed improved rheology, filtration, lubricity, and pore plugging ability (Mao et al., 2015). In addition, a variety of nano metallic oxide like CuO, ZnO, and TiO₂ was also investigated as an additive to improve performance of drilling fluids, especially at HTHT conditions (Cheraghian et al., 2013; Ponmani et al., 2015; William et al., 2014). Although these nanoparticles as additives in drilling fluids bring superior properties, most of they are expensive to prepare, nonrenewable, and nonbiodegradable. With more stringent control of pollution, safe risk, and cost, it is crucial to apply more environmental friendly and cost-effective nanoparticle as additives in drilling fluids.

Nanocellulose as an earth abundant, biodegradable, and renewable biopolymer nanomaterial receives great attention, due to its excellent characteristics such as nanoscale dimensions, high surface area to volume ratio, high mechanical strength/weight performance, and large flexibility (Habibi et al., 2010; Hartmann et al., 2016). It is extracted from various cellulosic resources like wood, cotton, chitin by mechanical treatment, acid hydrolysis, or enzymatic hydrolysis. Based on the morphology of nanocellulose, it can be categorized by cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs). CNCs show rod-like shape with several nanometers in width and 50-500 nm in length, while CNFs exhibit highly entangled
network and larger aspect ratio with 4-20 nm in width and several micrometers in length (Moon et al., 2011). The differences in the size and shape between them may lead to diverse interface effects which play an essential role in structure and properties of materials in study. The versatility of nanocellulose makes room for consideration in a wide range of revolutionary applications. It came into view of oilfield researchers and captured great interest judged by the related patents issued in the past several years. CNCs was added in well fluids to increase the viscosity of water-based well service fluids, such as kill pill, fracturing fluid, and gravel packing fluid, and improve the strength of cement (Rincon-Torres and Hall, 2013). CNCs from chitin was used as additives in cement and wellbore fluids to inhibit corrosion in pipelines and downhole tools (Hall, 2014). Additionally, CNCs were added in a variety of well fluids such as fracturing fluids, stimulation fluids, completion fluids, conformance control fluids, and drilling fluids for treating a subterranean formation by replacing conventional polymers in these fluids (Lafitte et al., 2015). The adding of nanocellulose as environmental friendly materials could reduce potential harmful effects on both drilling personals and the environment. These previous patents open the door to apply nanocellulose in drilling fluids, but further systematic work is required. Specifically, the size effects of nanocellulose on rheological and filtration properties of drilling fluids and characteristics of formed filter cakes, especially under HTHP conditions, are essential to fully in-depth understand functions of nanocellulose in the fluids.

In this study, a novel, low-cost, and ecologically friendly water-based drilling fluid containing nanocellulose, bentonite, and other additives including sodium hydroxide, lignite, polyanionic cellulose (PAC), and Rev dust were developed for enhancing drilling performance. The effect of nanocellulose morphology and concentrations on the rheological and fluid filtration properties of the drilling fluids were investigated. The fluid loss of the drilling fluids under low
temperature and low pressure (LTLP) and HTHP was measured and compared associated to the distinct microstructure of nanocellulose and their interactions with bentonite in the fluids. Special emphasis was placed on characteristics of formed filter cakes to demonstrate the effectiveness and performance of nanocellulose in the drilling fluids.

6.2 MATERIALS AND METHODS

6.2.1 Materials

Sulfuric acid and sodium hydroxide (ACS reagent) was purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA.). Wyoming sodium bentonite was provided by Baroid Industrial Drilling Products Inc. (Houston, TX, USA). Lignite was supplied from Halliburton (Houston, TX, USA). PAC was purchased from Halliburton Company (Houston, TX, USA). Rev dust was provided by Turbo-Chem International Inc. (Dr. Scott, LA, USA). Two types of nanocellulose were used in this study. One is CNFs (Celish KY 100-S grade, 25 wt% solid content) supplied by Daicel Chemical Industries, Ltd. (Tokyo, Japan). The other one is CNCs produced by breaking down the CNFs using acid hydrolysis. Specifically, the sulfuric acid (64 wt%) hydrolysis of the CNFs at 45 °C for 1 h followed by further mechanical separation by a high-pressure homogenizer (Microfluidizer M-110P, Microfluidics Corp., Newton, MA, USA) were applied to produce stable water suspensions of CNCs with an average concentration of 1.5 wt%. The surface morphologies of CNCs and CNFs were observed under a transmission electron microscope (TEM, JEOL 100 CX, Peabody, MA, USA).

6.2.2 Formations of Drilling Fluids

Water-based drilling fluids consisting of bentonite, nanocellulose, and other additives including sodium hydroxide, lignite, PAC, and rev dust were prepared to be as close as commercial drilling fluids under use in drilling fields. All the drilling fluids were prepared in a
standard 350 mL laboratory barrel. The concentrations of these components in the water-based drilling fluids were listed in Table 6.1. The contents of sodium hydroxide, lignite, PAC, and Rev Dust were constant for each experiment, and they were used as a pH control agent, deflocculant, filtration control agent, and substance of simulating drilled solids, respectively. Bentonite and nanocellulose varied from 10 g to 20 g and from 0.35 to 3.50 g in 350 mL water, respectively. For unit conversions, 1 g substance in 350 mL water is equal to 1 lb/bbl in field units.

### Table 6.1 Formulations of the drilling fluids

<table>
<thead>
<tr>
<th>Formulations</th>
<th>BT (^a) (g)</th>
<th>CN (^b) (g)</th>
<th>NaOH (g)</th>
<th>Lignite (g)</th>
<th>PAC (g)</th>
<th>Rev Dust (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT20</td>
<td>20</td>
<td>0</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>BT10</td>
<td>10</td>
<td>0</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>BT10/CN0.35</td>
<td>10</td>
<td>0.35</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>BT10/CN1.05</td>
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<td>1.05</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>BT10/CN1.75</td>
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<td>1.75</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>BT10/CN2.45</td>
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<td>2.45</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>BT10/CN3.50</td>
<td>10</td>
<td>3.50</td>
<td>0.25</td>
<td>1</td>
<td>0.5</td>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\) Bentonite; \(^b\) Nanocellulose including CNCs and CNFs

### 6.2.3 Rheological Measurements

Rheological properties of the drilling fluids were measured by an industrial rotating viscometer (NL Baroid, NL Industries, Inc., Houston, TX). The apparent viscosity (\(\mu_a\)), plastic viscosity (\(\mu_p\)), and yield point (\(\tau_y\)) were calculated using the following formulas according to American Petroleum Institute (API) recommended standard procedure of testing water-based drilling fluids.

\[
\mu_a = \theta_{600}/2 \quad (6.1)
\]

\[
\mu_p = \theta_{600} - \theta_{300} \quad (6.2)
\]
\[
\tau_y = \theta_{300} - \mu_p 
\]

where \( \theta_{300} \) and \( \theta_{600} \) were dial readings from the viscometer at a rotating speed of 300 and 600 rpm, respectively. To reach steady state conditions, the drilling fluids were stirred for 10 min prior to rheological measurements. In addition, the gel strength including \( Gel_{in} \) and \( Gel_{10min} \) of the drilling fluids was obtained by recording the maximum dial readings at 3 rpm after the fluid was stirred at 600 rpm for 1 min followed by maintaining static for 10 s and 10 min, respectively.

### 6.2.4 Fluid Filtration Testing

The LTLP filtration testing was conducted using a standard filter press with a regulated CO\(_2\) pressuring system and standard Fann filter papers (Fann Instrument Co., Houston, TX, USA). The measurements were completed at the pressure of \((100 \pm 5)\) psi \((3.9 \pm 0.35)\) bar) and the temperature of 25 \(\degree\)C according to American Petroleum Institute (API) recommended standard procedure of testing water-based drilling fluids. The mass of the filtrate against time was measured by a digital balance, and then the volume of filtrate was calculated by its mass and density. Thus, the API fluid loss versus time was determined. After the measurements, the filter cakes were removed from the cells and their thickness was recorded. Subsequently, these filter cakes were freeze-dried and coated with a thin layer of gold for observing their surface morphologies by a field emission scanning electron microscope (FE-SEM, FEI QuantaTM 3D FEG Dual Beam SEM/FIB, Hillsboro, OR, USA).

The HTHP filtration testing was completed by a permeability plugging apparatus (PPA) and ceramic discs (Fann Instrument Co., Houston, TX, USA). This equipment was designed to simulate field well conditions and these discs closely simulated the structure of formation, providing a more authentic representation of downhole filtration. A 300 mL sample of the drilling fluids was loaded into the PPA cell and a ceramic disc with an average pore throat
diameter of 20 μm was then inserted. The measurements were conducted at the pressure of 1000 psi and the temperature of 200 °F. The spurt loss ($V_3$) was recorded at the time when the pressure initially reached 1000 psi. The API fluid loss ($V$) was calculated by the following equation:

$$V = V_3 + (2 \times V_{30})$$

(6.4)

where $V_{30}$ was the fluid loss at 30 min. At the end of testing, thickness of the filter cakes deposited on the ceramic disks was recorded. Subsequently, the filter cakes were removed and the ceramic disks were dried and coated with a thin layer of gold prior to FE-SEM observation.

6.3 RESULTS AND DISCUSSION

6.3.1 Structure of Nanocellulose

![Figure 6.1 TEM photographs and diameter distributions (inserted plots) of the CNCs (A) and CNFs (B)](image)

The CNCs showed needle-like or whisker shaped morphology (Figure 6.1A), while the CNFs exhibited highly entangled network consisting of long nanofibers (Figure 6.1B). The CNCs have an average width of (8.2±2.3) nm and length of (321.6±34.7) nm, giving an aspect ratio of 39±15. The average diameter of CNFs was measured to be (18.6±6.9) nm and the length was much large in micrometers, compared to CNCs. Accordingly, the CNFs had wider distribution of diameters and higher aspect ratio than CNCs, resulting from the aggregations and large length of CNFs. In addition, it was worth mentioning that the sulfuric acid hydrolysis
introduced negatively charged sulfate groups onto the surface of CNCs, confirmed by the zeta potential and X-ray photoelectron spectroscopy analysis in our previous work (Li et al., 2015). These sulfate groups would resulted in more stabilized suspensions with individual CNCs well dispersed in them, compared to the CNFs without charged surfaces (Habibi et al., 2010). Due to these structural differences in dimension, shape, and surface characteristics between the CNCs and CNFs, it was expected that they would produce different effects on rheological and fluid filtration properties of the drilling fluids.

6.3.2 Rheological Properties

Drilling fluids are commonly considered as non-Newtonian fluids with viscosity decreases with increased shear rates (Bourgoyne et al., 1991). High viscosity of drilling fluids at low rates
was required to suspend drilled cuttings and carry them out of the wellbore, and low viscosity of drilling fluids at high rates made it easier for them to flow into downhole. Consequently, various additives were used to improve the rheological performance of drilling fluids (Abdo and Haneef, 2013; Hamed and Belhadri, 2009; Mahto and Sharma, 2004). The nanocellulose was thus added in drilling fluids due to its excellent rheological property, besides its abundance and environmental benefits. It was found that the water suspensions of nanocellulose showed obvious shear thinning behavior, with high viscosity at low shear rates and low viscosity at high shear rates (Moon et al., 2011). This phenomenon increased as concentration was raised and showed concentration dependence at low rates and reduced concentration dependence at high rates (Li et al., 2015; Moon et al., 2011). The effects of nanocellulose concentration on the rheological properties of the drilling fluids were shown in Figure 6.2 and Table 6.2. The control sample without nanocellulose exhibited significant shear thinning behavior, and its calculated values of apparent viscosity and plastic viscosity were 7.75 cP and 7.0 cP, respectively. When the bentonite content was reduced by half from 20 lb/bbl to 10 lb/bbl, the apparent viscosity and plastic viscosity of the fluids largely decreased with the values of 3.50 cP and 3.0 cP, respectively (Table 6.2). Maintaining the content of bentonite at 10 lb/bbl in the fluids, nanocellulose was added with its concentration varied from 0.35 to 3.50 lb/bbl. It was seen that the drilling fluids added with CNCs or CNFs still presented a marked shear thinning behavior similar to the control (Figure 6.2), confirming the non-Newtonian fluid properties of nanocellulose suspensions. Meanwhile, the viscosity went up with increased concentrations of nanocellulose in the fluids. When the content of nanocellulose increased to 1.05 lb/bbl, the apparent viscosity and plastic viscosity of the fluids added with CNCs were 6.75 cP and 6.0 cP and the corresponding values for CNFs were 8.75 cP and 6.5 cP, which more or less reached the
level of the control. By further increasing the concentration of nanocellulose, the viscosity, yield stress, and gel strength of the fluids continued to rise. Here, it was found that decreasing the content of bentonite and adding a small amount of nanocellulose, the rheological performance of the drilling fluids maintained and even be improved. This would be extremely beneficial because of the reduced solid content in the drilling fluids, which was preferred for faster drilling rate, decreased cost in solid control and fluid maintenance, reduced formation damage, and improved hydraulics (Mahto and Sharma, 2004).

Table 6.2 Rheological properties of the drilling fluids with different contents of nanocellulose

<table>
<thead>
<tr>
<th>Formulations</th>
<th>$\mu_\alpha$ (cP)</th>
<th>$\mu_p$ (cP)</th>
<th>$\tau_y$ (lb/100 sq ft)</th>
<th>Gel Strength (lb/100 sq ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gel$_{in}$</td>
</tr>
<tr>
<td>BT20</td>
<td>7.75</td>
<td>7.0</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>BT10</td>
<td>3.50</td>
<td>3.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BT10/CNC0.35</td>
<td>4.50</td>
<td>4.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BT10/CNC1.05</td>
<td>6.75</td>
<td>6.0</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>BT10/CNC1.75</td>
<td>9.65</td>
<td>6.8</td>
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<td>2.0</td>
</tr>
<tr>
<td>BT10/CNC2.45</td>
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<td>10.5</td>
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</tr>
<tr>
<td>BT10/CNC3.50</td>
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<td>18.5</td>
<td>8.4</td>
</tr>
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<td>BT10/CNF0.35</td>
<td>4.50</td>
<td>4.0</td>
<td>1.0</td>
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<td>34.05</td>
<td>12.4</td>
<td>47.3</td>
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</table>

The morphologies of nanocellulose played an essential role in the rheological properties of the drilling fluids. When the lowest amount (0.35 lb/bbl) of CNCs or CNFs was added, they had almost same values of apparent viscosity, plastic viscosity, yield point, and gel strength (Table
As the content of nanocellulose was above 0.35 lb/bbl, the rheological values (excluding Gel_{10min}) of the fluids with CNCs were lower than those of the fluids with CNFs and the differences between them became much larger with increased concentration of nanocellulose. For instance, at the nanocellulose concentration of 3.50 lb/bbl, the fluids with CNCs had apparent viscosity, plastic viscosity, yield point, and initial gel strength values of 20.75 cP, 11.5 cP, 18.5 lb/100 sq ft, and 8.4 lb/100 sq ft, respectively; whereas the corresponding values for the fluids with CNFs were 34.05 cP, 12.4 cP, 47.3 lb/100 sq ft, and 9.0 lb/100 sq ft, respectively. These differences were attributed to the distinct structure between CNCs and CNFs. The smaller size and well dispersion of the CNCs made them much easier to flow in the fluids under shear stress (Li et al., 2015). By contrast, the long fibers of CNFs formed a highly entangled network where the platelets of bentonite resided, and this system was much difficult to flow under the same shear stress. In addition, the Gel_{in} of the fluids with CNCs was slightly lower than that of the fluids with CNFs, but the Gel_{10min} reversed. The BT10/CNC3.50 had a Gel_{10min} value of 23.1 lb/100 sq ft, which was much larger than 9.5 lb/100 sq ft for the BT10/CNF3.50 (Table 6.2). This was due to the stronger hydrogen bonding properties of CNCs compared to CNFs. The surfaces of nanocellulose had hydroxyl groups which could form hydrogen bonding between these nanoparticles (Moon et al., 2011). Compared to CNFs, CNCs had a higher specific surface area because of their smaller dimensions, resulting in a larger number of hydroxyl groups available to form more hydrogen bonds. Accordingly, a stronger hydrogen bonding network was expected in the fluids with CNCs, making them much harder to flow. However, it took some time to build an effective hydrogen bonding network among CNCs in the fluids. The formed network was very weak within a very short time (10 seconds in this study) after a high speed of shear (600 rpm or 1022 s^{-1}). At this time, the gel strength (Gel_{in}) of the fluids with CNCs was still lower compared
to the fluids with CNFs. Giving a longer time (10 min), the stronger network with a larger number of hydrogen bonds was established, so much higher shear stress was required to initiate the flow of the fluids with CNCs. This kind of system was not built due to the limited hydroxyl groups of CNFs and larger dimensions, leading to the lower Gel$_{10\min}$ values of the fluids with CNFs (Figure 6.3).

![Figure 6.3 Schematic illustrating the formations of hydrogen bonding among CNCs and CNFs in the fluids](image)

6.3.3 Fluid Filtration Under LTLP

A preferred drilling fluid should have desired filtration properties such as a reasonable range of fluid loss as well as thin and dense filter cakes formed on the walls of wellbores, which could prevent fluid loss circulation, differential sticking, and even wellbore collapse (Bourgoyne et al., 1991). In Figure 6.4, the filtration volume of the drilling fluids under LTLP conditions against the square root of time was shown and linear relationships were observed. This could be explained by Darcy’s Law which was commonly used to describe the flow of drilling fluids filtrate through the filter cakes (Barry et al., 2015; Bourgoyne et al., 1991). The linear relationship between filtrate volume and square root of time was expected according to the solution to Darcy’s Law,
\[ V_f = \sqrt[2]{2\kappa \Delta p \left( \frac{f_{sc}}{f_{sm}} - 1 \right)} A \frac{\sqrt{t}}{\sqrt{\mu}} \]  

(6.5)

where \( V_f, t, \kappa, A, \Delta p, \mu, f_{sc}, f_{sm} \) is filtrate volume (mL), time (s), permeability (D), cross-section area (cm\(^2\)) of filter cakes, pressure drop across filter cakes (atm), viscosity (cP) of filtrate, volume fraction of solids in drilling fluids, and volume fraction of solids in filter cakes. The control (BT20) had a fluid loss of 12.47 mL, and the value increased to 15.36 mL when the bentonite content decreased to 10 lb/bbl (Table 6.3). After the nanocellulose was added, the fluid loss was slightly larger than BT20 but not obviously different from BT10, with varied values in the small ranges of 13.69-15.78 mL for the fluids with CNCs and 16.32-17.52 mL for the fluids with CNFs, respectively. This indicated that the concentration of nanocellulose didn’t have a significant effect on the filtrate volume of the drilling fluids under LTLP conditions. Additionally, it was noticed that the fluid loss of the fluids with CNFs was a little higher than that of the fluids with CNCs, which would be explained by further investigating the formed filter cakes.

![Figure 6.4 Filtration volume versus square root of time for the drilling fluids under LTLP conditions](image)

Figure 6.4 Filtration volume versus square root of time for the drilling fluids under LTLP conditions
Table 6.3 The API fluid loss, thickness, and permeability of filter cakes for the drilling fluids under LTLP conditions

<table>
<thead>
<tr>
<th>Formulations</th>
<th>$V_f$ (mL)</th>
<th>$h_c$ (cm)</th>
<th>$k$ (μD)</th>
<th>$k/h_c$ (μD/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT20</td>
<td>12.47</td>
<td>0.13</td>
<td>2.32</td>
<td>17.8</td>
</tr>
<tr>
<td>BT10</td>
<td>15.36</td>
<td>0.10</td>
<td>2.17</td>
<td>21.7</td>
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<td>BT10/CNC0.35</td>
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<td>0.10</td>
<td>1.94</td>
<td>19.4</td>
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<tr>
<td>BT10/CNC1.05</td>
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<td>0.10</td>
<td>2.55</td>
<td>25.5</td>
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<td>BT10/CNC1.75</td>
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<td>BT10/CNC2.45</td>
<td>15.34</td>
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<td>3.46</td>
<td>21.6</td>
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<tr>
<td>BT10/CNC3.50</td>
<td>14.46</td>
<td>0.27</td>
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<td>BT10/CNF0.35</td>
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<tr>
<td>BT10/CNF3.50</td>
<td>17.35</td>
<td>0.32</td>
<td>7.45</td>
<td>23.3</td>
</tr>
</tbody>
</table>

The characteristics of filter cakes were shown in Table 6.3 and Figure 6.5. The thickness of filter cakes for BT20 and BT10 was 0.13 cm and 0.10 cm, respectively. When a small content (<1.75 lb/bbl for CNCs and <1.05 lb/bbl for CNCs) of nanocellulose was added into the fluids, the thickness of filter cakes almost unchanged within the values of 0.10-0.11 cm. As more nanocellulose was used, the thickness of filter cakes increased quickly and reached to 0.27 cm for BT10/CNC3.50 and 0.32 cm for BT10/CNF3.50. The similar trend was found for the permeability of the filter cakes calculated by the following equation,

$$\frac{dV_f}{dt} = \frac{\kappa A \Delta p}{\mu h_c}$$  \hspace{1cm} (6.6)

where $h_c$ is the thickness of filter cake (cm). To calculated the permeability, $A$, $\Delta p$, and $\mu$ were assumed to be constant with the values of 45 cm$^2$, 690 Pa, and $1\times10^{-3}$ Pa·s, respectively.
The increased thickness and permeability of filter cakes with larger amount of nanocellulose (>1.75 lb/bbl for CNCs and >1.05 lb/bbl for CNFs) resulted from more loose structure of cakes caused by the added nanofibers, especially for CNFs (Figure 6.5). These nanofibers and bentonite were not miscible and the interfaces between them could offer paths for the filtrate to flow through the filter cakes and enhanced the connectivity of pores in the filter cakes. This phenomenon became more obvious with increased concentration of nanocellulose and larger nanofibers, resulting in relatively larger permeability of filter cakes with CNFs compared to CNCs. In addition, filtrate volume was proportional to permeability but inversely proportional to thickness of filter cakes according to the above equation. Then, the ratio of permeability to cake thickness was calculated and found to fit well with the values of filtrate volume (Table 6.3). Consequently, the slightly higher fluid loss of the drilling fluids with CNFs compared to the fluids added by CNCs was contributed by both the increased permeability and thickness of filter cakes, but the former made a bigger one than the later.

Figure 6.5 Surface and cross sectional FE-SEM images of the filter cakes for BT20 (A and D), BT10/CNC3.50 (B and E), and BT10/CNF3.50 (C and F) under LTLP conditions (A, B, and C: Cross section morphology; D, E, and F: Surface morphology)
6.3.4 Fluid Filtration Under HTHP

The API fluid loss and cake thickness of the drilling fluids under HTHP conditions were shown in Figure 6.6. The control (BT20) had a filtrate volume of 50 mL at the end of 30 min testing time. When the bentonite content decreased by half, the filtrate spurted out quickly and continuously and the applied pressure could not go up to 1000 psi, making the measurement of fluid loss for BT10 unattainable. This indicated that 10 lb/bbl of bentonite in the fluids was not enough to plug the pores (diameter 20 μm) of the ceramic disks in this study. However, this situation was avoided by adding nanocellulose into the drilling fluids with 10 lb/bbl of bentonite. The fluid loss decreased with increased concentrations of nanocellulose. As the CNFs were above 1.05 lb/bbl, the filtrate volume of the fluids was even lower than that of the control sample, with values ranging from 36-47 mL depending on the amount of CNFs. In addition, the fluids with CNFs performed much better than those with CNCs, although the former had a little higher thickness of filter cakes than the later. The differences in filtrate volume between the fluids added with CNCs and CNFs were related to their different pore plugging ability under HTHP conditions.
Figure 6.7 Surface and cross sectional FE-SEM images of the ceramic disks for BT20 (A and D), BT10/CNC3.50 (B and E), and BT10/CNF3.50 (C and F) under HTHP conditions (A, B, and C: Cross section morphology; D, E, and F: Surface morphology)

The penetration of the drilling fluids into the porous ceramic disk was shown in Figure 6.7. It was seen that the solids mainly entered into the surface of the disks with a depth of 100-300 μm. Compared to BT20, the fluids added with nanocellulose had a lower penetration depth, due to the reduced solid contents in the drilling fluids. The fluids with CNCs could not seal the pores in the disks completely because of their very small dimensions. On the contrary, the fluids with CNFs plugged the pores more efficiently with their long entangled fibers, contributing to the lower fluid loss of the drilling fluids with CNFs. Therefore, a decreased amount of bentonite from 20 lb/bbl to 10 lb/bbl with addition of a small fraction of CNFs (1.05-3.50 lb/bbl) could reduce the fluid loss and formation damage with a less penetration depth. Additionally, it was worth mentioning that the effect of nanocellulose on pore plugging ability was dependent on the size of itself and pores of disks. Therefore, the size of nanocellulose could be tuned by changing
the preparation conditions such as concentrations of sulfuric acid and time of acid hydrolysis to maximize the plugging capability for subsurface formations with different pore diameters.

6.4 CONCLUSIONS

The novel low cost, ecologically friendly, and high performance water-based drilling fluids were successfully fabricated by replacing half of bentonite in traditional fluids with earth abundant nanocellulose. The added nanocellulose played an essential role in improving the rheological and fluid filtration properties of the drilling fluids. The fluids with nanocellulose showed similar non-Newtonian fluid behavior to the control, due to the excellent shear thinning properties of water suspensions of nanocellulose. The viscosity, yield point, and gel strength of the fluids increased with an increasing concentration of nanocellulose. The fluids with CNCs were easier to flow due to their small dimensions and well dispersions than the fluids added by CNFs having long and highly entangled nanofibers, resulting in lower values in viscosity, yield point, and initial gel strength for the former compared to the later. The high 10-min gel strength of the fluids with CNCs was attributed to the strong hydrogen bonding network formed among CNCs. For filtration properties, the fluid loss of the drilling fluids added with nanocellulose was larger than the control under LTLP conditions, due to the enhanced connectivity of pores in the filter cakes by the nanocellulose. However, the nanocellulose performed much better under HTHP conditions, especially the CNFs. The long and highly intertwined CNFs plugged the pores in the ceramic disks efficiently, leading to lower fluid loss even than the control when the content of CNFs was above 1.05 lb/bbl. Furthermore, the dimensions of nanocellulose could be controlled to maximize the plugging effect of subsurface formations with different pore sizes. Therefore, a novel pathway was provided to develop novel renewable biopolymer additives in
water-based drilling fluids with enhanced performance and advantages of low cost and ecologically friendly.

6.5 REFERENCES


CHAPTER 7 OVERALL CONCLUSIONS

7.1 MAIN CONCLUSIONS

In this study, biomass resources (tar and nanocellulose) were utilized to prepare low-cost nanocomposite and drilling fluids. On one hand, tar from biomass gasification was recycled for fabricating low-cost antimicrobial nanofiber by electrospinning. On the other hand, nanocellulose was used as a “green” additive in drilling fluids for improving rheological and fluid filtration properties. The conclusions of this study are as follows:

The tar was a complex mixture mainly composed of highly branched PAHs, furans, aliphatics, and esters as indicated by the GC-MS and FTIR spectroscopy. The elemental analysis showed that biomass tar with higher H/C and O/C was more oxygenated and less aromatic than fossil pitches, implying that the tar was more reactive. The complex composition of the tar led to a broad thermal decomposition temperature range. The tar decomposed at a low temperature (183-252 °C depending on the heating rates) compared with biomass feedstock, due to the low molecular mass components in the tar produced by gasification. The thermal kinetics of the tar indicated that single reaction mechanism can be applied in low conversion rates and the reaction mechanism changed in higher conversions caused by the complex reactions in decomposition process of biomass tar.

The tar and PAN was blended and electrospun into nanofibers. The contents of tar in the blends significantly affected the morphology, thermal properties, pore characteristics, and antimicrobial activity of the resulting electrospun nanofibers. Continuous nanofibers were produced at the tar content levels up to 100 wt% based on the weight of PAN. The tar/PAN nanofibers exhibited increased average diameters and surface roughness with increasing content of tar. ATR-FTIR spectroscopy revealed that the tar was successfully incorporated into the
The tar/PAN nanofibers were less thermally stable than the neat PAN nanofibers due to the relatively low onset temperature of degradation of biomass tar, and their thermal stability decreased with increasing amount of tar. However, the tar/PAN nanofibers had a comparable amount of residual weight (35%) compared to PAN (38%) at 600 °C, suggesting that tars can be an attracting precursor for manufacturing carbon nanofibers. Furthermore, the addition of tar facilitated catalytically the cyclization of PAN, which is helpful for stabilization processes in the manufacture of PAN-based carbon fibers. The tar/PAN nanofibers exhibited increased antimicrobial capacity against *S. aureus* and *E. coli* with increased tar content.

Continuous microporous CNFs from biomass tar/PAN/silver hybrids with antimicrobial capabilities were fabricated through electrospinning and subsequent thermal stabilization and carbonization. Silver nitrate was reduced to silver nanoparticles, which conferred the antimicrobial abilities to the as-spun nanofibers and CNFs. The as-spun nanofibers showed larger average diameters with increased tar loading levels, due to larger concentrations of tar and PAN in the suspensions. However, the increased contents of tar made the fiber surface rougher and increased fiber diameter variations resulted from tar aggregations and phase separations between tar and PAN. In addition, the incorporation of tar reduced the thermal stability of the as-spun nanofibers due to relatively lower onset degradation temperatures of the tar components. The tar also slowed down the cyclization reactions of PAN by its ionizable groups, which was helpful for subsequent stabilization processes. The as-spun nanofibers exhibited mesopore characteristics while micropores dominated in the CNFs due to the combined effects of thermal decompositions of some tar constituents and phase separations of tar and PAN. The large specific surface areas and the volumes of pores of the as-spun nanofibers and CNFs made the
silver nanoparticles more easily diffuse into the broth, endowing their excellent antimicrobial abilities.

In addition, the low solid drilling fluids were successfully prepared by substituting nanocelulose (CNCs and CNFs) for a part of bentonite in the fluid system. Both the CNC-DF and CNF-DF exhibited similar pseudoplastic behavior, due to the excellent shear thinning characteristics of CNP suspensions. Additionally, the viscosity, yield point, and gel strength of the drilling fluids decreased with additions of CNPs. In comparison, the CNC-DF fluids had lower values of viscosity, yield point, and gel strength than CNF-DF, attributed to their distinct structure characteristics and different interactions with bentonite in the fluid system. On the other hand, the filtrate volume of the drilling fluids increased with an increasing content of CNPs, and no significant difference in standard fluid loss was found between CNC-DF and CNF-DF. However, the filter cakes of CNC-DF showed lower values of thickness and permeability but higher porosity, compared to CNF-DF. The high porosity and low permeability of the filter cakes from CNC-DF were attributed to isolated pores formed by the aggregation and separation of CNCs and bentonite. The flexible 3D network of CNFs bound more bentonite particles closely, resulting thicker filter cakes with lower porosities. Meanwhile, the CNFs provided the paths of filtrate flow and increased the pore connectivity in the filter cakes, contributing to its higher permeability. The rheological and fluid filtration properties of CNP added drilling fluids could be further optimized by tailoring the size distributions and surface functionality of CNPs.

Finally, nanocellulose was added into the water-based drilling fluids composed of reduced amount of bentonite as well as other additives, which simulated the fluids under field use. The added nanocellulose played an essential role in improving the rheological and fluid filtration properties of the drilling fluids. The fluids with nanocellulose showed similar non-Newtonian
fluid behavior to the control, due to the excellent shear thinning properties of water suspensions of nanocellulose. The viscosity, yield point, and gel strength of the fluids increased with an increasing concentration of nanocellulose. The fluids with CNCs were easier to flow due to their small dimensions and well dispersions than the fluids added by CNFs having long and highly entangled nanofibers, resulting in lower values in viscosity, yield point, and initial gel strength for the former compared to the later. The high 10-min gel strength of the fluids with CNCs was attributed to the strong hydrogen bonding network formed among CNCs. For filtration properties, the fluid loss of the drilling fluids added with nanocellulose was larger than the control under LTLP conditions, due to the enhanced connectivity of pores in the filter cakes by the nanocellulose. However, the nanocellulose performed much better under HTHP conditions, especially the CNFs. The long and highly intertwined CNFs plugged the pores in the ceramic disks efficiently, leading to lower fluid loss even than the control when the content of CNFs was above 1.05 lb/bbl. Furthermore, the dimensions of nanocellulose could be controlled to maximize the plugging effect of subsurface formations with different pore sizes. Therefore, a novel pathway was provided to develop novel renewable biopolymer additives in water-based drilling fluids with enhanced performance and advantages of low cost and ecologically friendly.

7.2 FUTURE WORK

Due to the relatively high carbon content in biomass tar, it is a promising materials for carbon materials, including carbon fibers, porous carbon, and carbon foam. Different carbon materials have been fabricated and characterized using coal or petroleum derived pitch which has a similar composition to tar. However, carbon materials produced by tar from biomass conversions have not been reported. Consequently, it is expected to manufacture biomass tar-based carbon materials using this abundant and low-cost carbon precursor. In this study, the
Biomass tar derived carbon fibers were prepared by electrospinning with PAN. The obtained showed porous structure that showed potential in a wide of applications, including absorption, separation, and filtration. Continued work could be done to measure the performance of the fabricated tar-derived carbon in these applications. In addition, the biomass tar could be also used to produce porous carbon and carbon foam materials. The synthesis of porous carbon materials can be achieved by various methods, including chemical or physical activation, catalytic activation, carbonization of polymer blends containing thermally decomposable components, carbonization of a polymer aerogel, and templating method. These porous carbons provide unique benefits such as high specific surface area and large porosity in combination with good chemical and mechanical stability, which can be widely used in applications such as gas separation, water purification, catalyst supports, and electrodes for electrochemical double layer capacitors and fuel cells. In addition, carbon foam can be produced from a carbon precursor under high pressure or made by introducing gas bubbles into the liquid resin, allowing the bubbles to grow and stabilize, solidifying and then carbonizing. Through these work, the tar-associated environmental damage can be reduced and the efficiency of biomass utilization can be also largely improved.

For the application of nanocellulose in fluids for oil and gas exploitation, future work could be continued to use nanocellulose as a functional additive in fracturing fluids. The traditional fracturing fluids are mainly formulated by guar gum whose price increases a lot in recent years. A cheaper substitute for guar gum is high desirable to reduce the cost of oil and gas production. Nanocellulose is a promising candidate due to its excellent characteristics such as good rheological properties and eco-friendliness. Little work has been done in application of nanocellulose in fracturing fluids until now. The rheology of nanocellulose crosslinked by borax,
crosslinking mechanism by different crosslinkers, the interactions between guar gum and nanocellulose, the suspending capability of fluids added with nanocellulose will be the interesting research spots.
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VITA

Kunlin Song was born in Sichuan Province, China. He obtained the BS in Wood Science and Engineering from Beijing Forestry University, Beijing, China, in 2009. He got his MS Wood Science and Technology from Chinese Academy of Forestry, Beijing, China, with Dr. Yafang Yin as advisor, in 2012, where he studied wood cell wall polymers (cellulose, lignin, and hemicellulose). Since 2012, he has studied in School of Renewable Natural Resources at Louisiana State University as a Ph.D candidate with Dr. Qinglin Wu as advisor. His research focuses the preparation, characterization, and application of electrospun nanofibers and composites. He anticipates graduating with his Ph.D degree in August 2016.