OXIDATIVE REACTIONS OF PEANUT HULLS

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

By

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

APOS	alkaline peroxide oxidation system
FT-IR	Fourier transform infrared
HD	high density
LD	low density
Red-ox	Reduction/oxidation
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TSOS	TEMPO selective oxidation system
UM	unmodified
UV-Vis	Ultraviolet-visible

ABSTRACT

OXIDATIVE REACTIONS OF PEANUT HULLS

Michael Jason Sands, Masters of Science in Chemistry
Western Carolina University (April 2020)
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This study investigates how a variety of oxidants can be used to chemically modify ground peanut hulls. Low density and high density hulls were modified using three different oxidizing environments: an alkaline peroxide oxidation system (APOS), potassium permanganate, and a selective oxidizing system containing (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO). Reactions with cellulose were also carried out as a control. Temperature, oxidation-reduction potential and pH were monitored for the duration of the modifications. Infrared (IR) spectra were acquired of unmodified and modified samples to probe chemical changes in the hulls. The selective TEMPO and non selective permanganate oxidation systems show that an oxidizing environment is not responsible for the modification of the peanut hulls observed in the APOS. IR spectra reveal that oxidation in not occurring between the hulls and the APOS reaction, or any other modification. Rather, something that is alkaline soluble within the hulls dissolves into solution effecting the adsorption capacity of them.

CHAPTER ONE: INTRODUCTION

Background

Industries such as textiles, mineral processing, metal plating, electric and chemical plants produce waste water that contain ionic dyes and dissolved heavy metals that are toxic, carcinogenic, and mutagens that require removal from effluent before being released back into water ways and the environment.[1,2] Waste water treatment is costly due to the amount of water needing to be purified and the expense of replacing ionic exchange resins or activated charcoal.[1]

The use of readily available natural products such as wheat straw, rice husk, coir piths and peanut hulls as opposed to synthetic resins and membrane filters would lower the cost of waste water treatment.[3,4] Jute fibers[5,6] and peanut hulls,[7] due to their lignocellulosic structure comprised of the monomers in Figure 1, have been shown to adsorb cations with and without modifications to the surface of the fibers.[5,8] In jute fibers, a bleaching process involving sodium hydroxide and hydrogen peroxide caused an increase in adsorption capacity for nickel(II), copper(II), and zinc(II) which has been attributed to the formation of carboxylic acid groups due to oxidation of functional groups on the fiber's surface.[5] Peanut hulls have a similar lignocellulose structure and have been modified in other alkaline solutions.[8,9]

Hulls have the ability to adsorb heavy metals and are of interest as a biosorbent material due to their availability and the current need for a cheaper alternative to ion-exchange resins.[10] This medium can then be disposed of in sanitary landfills or even rejuvenated and reused. Ground peanut hulls can be separated based on their density.[11] Low density (LD) hull particles float in water, whereas high density (HD) hull particles sink. The adsorption capacity of both types of hulls increases when hulls are modified using a modification bath that is alkaline.[8,11] Both unmodified and modified LD hulls have a higher adsorption capacity than HD hulls.[12] This higher adsorption capacity is likely due in part to increasing surface area by dissolution of alkaline soluble material, presumably lignin, present in the hull's structure.[12]

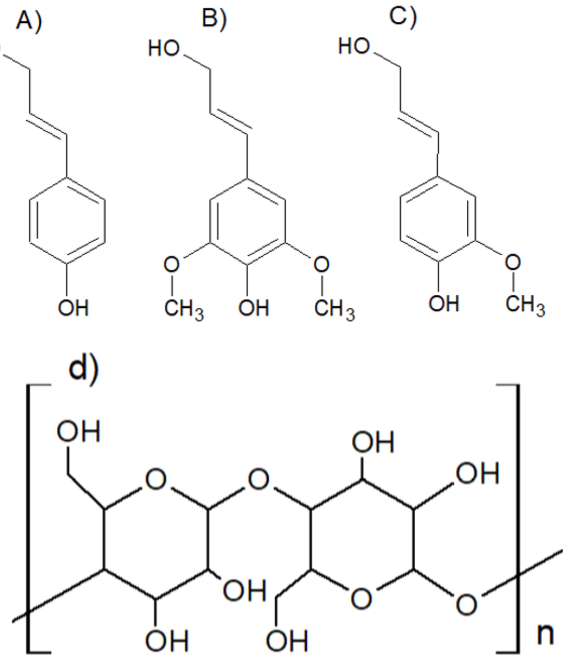


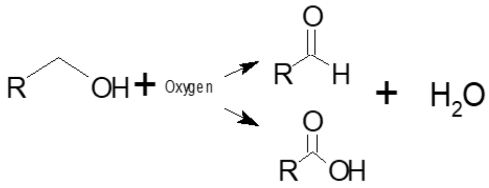
Figure 1. Chemical structures of (a) coumaryl alcohol, (b) sinapyl alcohol, (c) coniferyl alcohol, the monomers that make up lignin, and (d) cellulose.

Goals and Methodology

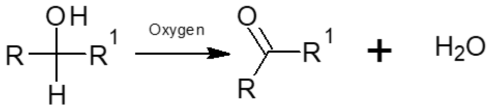
The goal of this research is to determine the chemical differences among HD and LD peanut hulls, as well as any.chemical differences that occur as a result of an oxidizing environment. Three different oxidizing environments were selected for this study. and alkaline oxidative system (APOS) was selected since previous studies showed this modification enhances adsorption capacity in both jute fibers[5] and peanut hulls.[12] Potassium permanganate was selected because it is a known strong oxidizer. It was assumed that if oxidation were to occur in the hulls, it would be maximized by the use of this nonselective oxidizing agent. Lastly, a selective oxidizing agent, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was used because under varying conditions it can selectively oxidize primary alcohols. Cellulose withing the peanut hulls contain both primary and secondary alcohols, and the TEMPO selective oxidation system (TSOS) could aid in the interpretation of the results if only some alcohol groups were converted. Unmodified and modified cellulose is also studied as a control since its structure is well known. Determining the chemical differences between modified and unmodified HD and LD hulls within the lignocellulosic structure can be probed using information rich Fourier transform-infrared (FT-IR) spectroscopy. The results of this study can help to drive optimization of the modification process to increase hulls' ability to adsorb heavy metals. The results may also elucidate binding/adsorption mechanisms. The APOS and $KMnO_4$ are strong oxidizers, which would result in the conversion of alcohols to carboxylic acids (or carboxylate anions in the presence of base) and ketones.

Chemical changes that occur within the hulls as a result of an oxidizing environment can be probed by monitoring the pH, temperature and oxidation-reduction potentialof the oxidizing reactions. The primary alcohols present in the hulls (Figure 1) could be converted to either aldehydes with milder oxidizing conditions, or carboxylic acids when over oxidized. Scheme 1 shows the production of carbonyls that could result from the reaction of secondary alcohols within the lignin or cellulose.

On the other hand, the TSOS selectively oxidizes primary alcohols to carboxylic acids, leav-



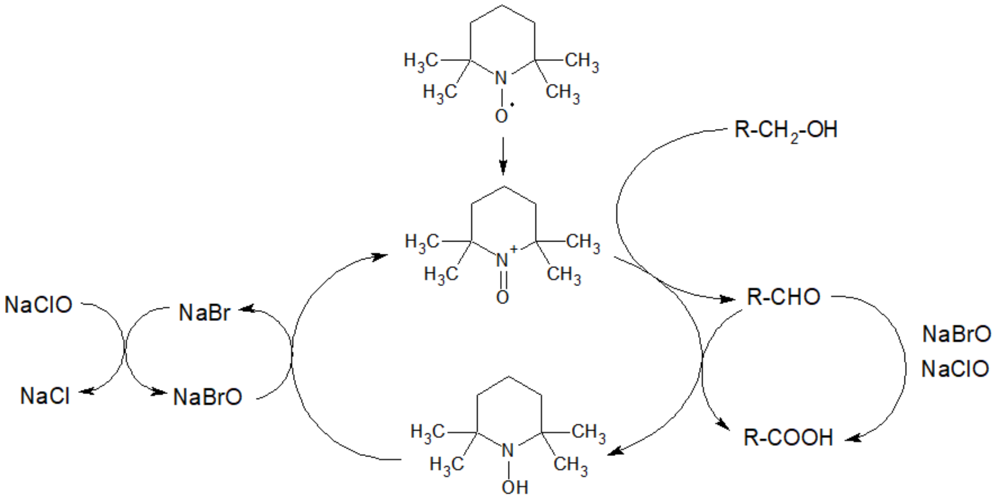
Scheme 1. Oxidation products expected from mild oxidation (top) and over oxidation (bottom) of a primary alcohol.



Scheme 2. Oxidation products expected from oxidation of a secondary alcohol.

ing secondary alcohols unreacted. The reaction mechanism in Scheme 3 shows how the TEMPO radical will mediate the oxidizing process by acting as an oxoammonium salt under basic conditions in the Anelli oxidation, the TEMPO is recharged as a piperdine-oxyl by a bromide ion carrying an oxygen provided by the chlorite or other oxygen source, and it continues to perform oxidation catalytically.[13] Previous Anelli oxidation of cotton and ramie fibers using TSOS showed that carboxylic acid groups can be observed if there is a successful reaction.[6,14] Reaction conditions and a spectral analysis of the hulls is used to determine if any of these reactions are occuring under a variety of oxidative conditions.[15] Also in the presence of an oxidizing agent, the double bonds present in the lignin could undergo a dihydroxylation if over oxidized, the bond can become cleaved, yielding two substituted aldehydes as in Scheme 4.[16]

Previous Anelli oxidation of cotton and ramie fibers using TSOS showed that carboxylic acid groups can be observed if there is a successful reaction.[6,14] Reaction conditions and a spectral analysis of the hulls is used to determine if any of these reactions are occuring under a variety of oxidative conditions.[15] Also in the presence of an oxidizing agent, the double bonds present



Scheme 3. Anelli oxidation mechanism of the TSOS.

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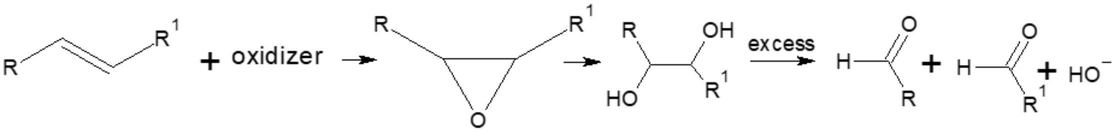

Scheme 4. Products expected from dihydroxylation of double bonds followed by bond cleavage and over oxidation of the resulting alcohols.

The pH, temperature, and oxidation reduction potential (ORP) can be monitored during the reactions. The pH tells us whether or not the alkalinity changes as hulls are allowed to react with different oxidizers. For example, in the reaction depicted in Scheme 4, hydroxide is a by-product, so an increase in pH and decrease in temperature could indicate the production of hydroxides in solution.[16] The temperature can indicate if an endothermic or exothermic reaction is taking place, and the ORP will indicate relative amounts of direct electron transfer.[17] A positive ORP indicates a high concentration of electrons in solution, pulling electron density away from the probe.[17] The stronger the oxidizer, the higher the ORP will be.[18] A decrease in ORP would indicate chemical species in the reaction are becoming oxidized.[18,19]

In addition to monitoring the modification reactions, an analysis of the hulls before and after the reaction can reveal any chemical changes within the hulls. These changes can be probed using Fourier transform infrared (FT-IR) spectroscopy. Specifically spectral differences could illuminate which functional groups are modified within the hulls (if any). For instance, infrared bands of interest include those associated with carbonyls, primary, and secondary alcohols. The carbon-oxygen double bond for carbonyls and carbon oxygen single bonds for primary and secondary alcohols appear in the IR spectrum at (1700 cm^{-1}, 1130 cm^{-1}, 1080 cm^{-1}, respectively).[4] These alcohol groups are present throughout the lignocellulosic structure of the hulls and are targets for modification via oxidation while carbonyls are potential oxidation products. With these possible products, the bands between 1700 cm^{-1} and 1730 cm^{-1} will be of the most interest.

Lastly, after modification, the solution bath can also be examined for water soluble products using UV-Vis spectroscopy. Absorption bands in the ultraviolet range would indicate the presence of any conjugated compounds that may have been dissolved into the reaction bath during the modification. The compounds undergo $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions that absorb light with a wavelength range of 250 - 350 nm.[20] Lignin in the hulls is a source of conjugated compounds.

CHAPTER TWO: EXPERIMENTAL

Peanut Hull Preparation

Peanuts and seed coats were removed from the hull. Hulls were then placed into a Hamilton Beach coffee grinder (Fresh Grind 80335). After grinding for approximately 30-45 s, the contents were placed into sieves. Two 8 in diameter USA Test Sieves (Fisherbrand) with 1 mm and 0.5 mm mesh were stacked with a catch basin below onto a Gilson Sieve Shaker (model SS15-7529) and set to shake for 3-5 min. The hulls that did not pass through the first sieve were reground and sieved again, while the hulls retained by the 0.5 mm sieve were collected and saved for modification and analysis.

Ultrapure water from Thermo Scientific brand nano purification system (model 7719) was boiled and then poured over the hulls. The mixture was stirred and allowed to sit for 5 min. Hulls were then filtered and rinsed with cold ultra-pure water. The hulls were then dried in a 50 °C oven. Hulls were separated by density via decantation in ultrapure water. The low density hulls floated to the top and were decanted into a Büchner funnel attached to a vacuum. The remaining high density hulls were filtered separately. Hulls were dried for a second time at 50 °C. Different reactions were carried out on these sets of hulls or used as unmodified samples (UM). For all reactions, temperature, ORP, and pH were monitored using Vernier probes and LoggerPro software set to sample every 30 s for 24 h.

Alkaline Peroxide Oxidation System

The alkaline peroxide oxidation system (APOS) contained 100 mL of 0.95 M NaOH mixed with cold 30% H_2O_2, both from Fisher Scientific. The reaction mixture was added to a water jacketed beaker attached to a Thermo Scientific Isotemp cold water bath regulator set to 20 °C. This beaker was set into a secondary container on a stir plate. Lastly, 2 g of material to be modified were added with a stir bar set to a low stir rate. This reaction produces foam, so nylon netting was placed over the jacketed beaker using rubber bands to retain the hulls. The water bath regulator was maintained at 20 °C for the first 2 h of the reaction and then the reaction continued with the regulator turned off. After 24 h of total reaction time, the hulls/cellulose were then vacuum filtered and rinsed with ultrapure water until the pH of the wash water was neutral. After filtration, these hulls were allowed to dry in a 50 °C oven overnight.

Potassium Permanganate Oxidation

A 100 mL solution of 0.01 M $KMnO_4$ (J.T Baker Chemical Co.) was prepared and 2 g of hulls or cellulose were added and allowed to react at room temperature for 24 h. The hulls or cellulose were vacuum filtered and rinsed with ultrapure water until the rinse water ran clear. A small portion of hulls was rinsed in a 5% nitric acid, and the rinse was analyzed using flame atomic absorption spectroscopy (FAAS) to qualitatively assess the presence of manganese on the hull surface.

Selective Oxidation

A 100 mL solution containing 10 mmol (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (Sigma-Aldrich), and 10 mmol of sodium bromide (Fisher) was prepared by first adding TEMPO and sodium bromide to a 100 mL volumetric flask and then diluting to volume using ultrapure water. This mixture was sonicated for 15 minutes to ensure TEMPO was dissolved and transferred to a beaker. A solution of sodium chlorite was made by adding ultrapure water to 2.5 mmol of the chlorite until total mass reached 5 g. The material to be modified (2 g) was added to the TEMPO/NaBr mixture on a stir plate. To this mixture, all of the chlorite solution was added to start the reaction. The TEMPO selective oxidation system (TSOS) modification was carried out for 24 h at room temperature. This system favors products more at pH of 11 [14,21] and so the pH was adjusted using 0.05 M NaOH. Oxidation was terminated by the addition of 2 mL of 95% ethanol for approximately 5 min. Modified material was recovered via vacuum filtration and rinsed excessively with ultrapure water to remove excess solute ions from the material as suggested.[21]

Effects of pH on Modified Material

Previous adsorption experiments[12,22] were carried out in pH 4 phthalate buffer prepared from pHydrion buffer capsules (Fisher), because adsorption capacity is high in acidic conditions. To explore any effects of pH on the chemical state of the hulls in this study, a sample of each modified material was soaked in pH 4 buffer. Each buffer solution was made with ultra-pure water in a 100 mL volumetric flask in accordance with the manufacturer's directions.

FT-IR Analysis of Material

Infrared spectra of all unmodified and modified materials were acquired with an infrared microscope (Nicolet Centarus). Six spectra were acquired for each sample. For hulls, three spectra were acquired from each side of the hull. The mercury cadmium telluride detector was set for 64 scans per measurement and background scans. Background scans were performed before each measurement with a range of 650-4000 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were plotted in Log(1/R) format. These spectra were exported as JDX files and processed using Python 3.6 software in a Jupyter notebook. These spectra were compiled into a data frame, cropped to 700 cm^{-1}-3900 cm^{-1} , normalized to a peak at 1170 cm^{-1}, and then the replicate spectra of each sample were averaged together to yield one spectrum for each sample.

UV-Vis Analysis of Reaction Solutions

A reaction solution from an APOS LD modification was measured using an Agilent 8453 UV-Vis Spectrometer, set to observe wavelengths from 400 to 800 nm. Water was used as the blank.

CHAPTER THREE: RESULTS AND DISCUSSION

Physical Description

Figure 6 shows the appearance of the hulls and cellulose before and after modification. Both low density (LD) and high density (HD) hull types show a lighter appearance after being modified by the alkaline peroxide oxidation system (APOS), while the cellulose seems unchanged in color. All materials show a darkening of the surface when modified by $KMnO_4$, including the cellulose. The darkening in this case was suspected to be a coating of manganese dioxide or manganese oxide which may have been coated onto the material's surface. The materials were soaked in a 5% nitric acid solution in an attempt to dissolve any metal oxide coating. The resulting materials were lighter in color, and a flame atomic absorption spectroscopy of the nitric acid solution qualitatively confirmed the presence of manganese. The (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) selective oxidizing system (TSOS) modified material shows no color change, or any other change to their physical appearance.

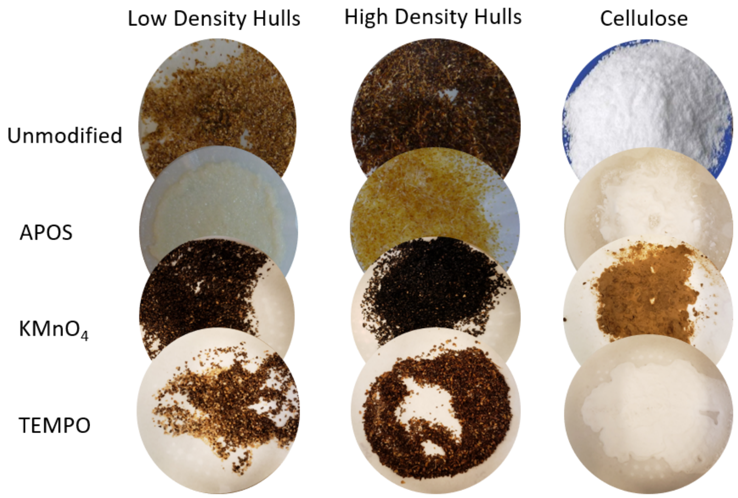

Figure 2. LD hulls, HD hulls and cellulose before and after different modification reactions.

Alkaline Peroxide Oxidation System Modifications

Hulls and cellulose were modified using an alkaline peroxide oxidative system (APOS) containing hydrogen peroxide and sodium hydroxide. For comparison, a control reaciton was also carried out in which no hulls or cellulose were present. Figure 3 shows that the control reaction and cellulose reaction both have a similar increase in pH, a decrease in oxidation-reduction potential (ORP) and a small increase in temperature. The similarity between these two reaction profiles suggests that the cellulose is not modified by the APOS, and the change in pH, temperature, and ORP are presumably due to a reaction between NaOH and H_2O_2.[23]

At each step, heat is produced as water and oxygen are formed. This reaction can explain the increase in temperature, the increase in pH, and redox chemistry observed in the APOS reaction. The pH increase is the same for all three reactions and the control, starting at around 10 and ending at 14. The increase happens faster when hulls are present though. A proposed mechanism for this decomposition as it occurs in base is shown below:[24,25]

$$(1) \quad H_2O_2(aq) + OH^-(aq) \rightleftharpoons HO_2{}^-(aq) + H_2O(l)$$

$$(2) \quad H_2O_2(aq) + HO_2{}^-(aq) \rightleftharpoons H_2O(l) + O_2(g) + OH^-(aq)$$

The HD hulls show the greatest change in temperature with a maximum temperature at 66.5 °C. This large temperature change could indicate a possible reaction between the sodium hydroxide, hydrogen peroxide, and a component in the hulls such as lignin.[26] This is supported by the much smaller change for the control bath and the cellulose in which no lignin is present. One possible "reaction" is the dissolution of lignin or other base soluble hull components. Removal of material is consistent with an increase in empty space seen in hulls after this type of modification observed previously.[12]

The UV-Vis absorption spectra in Figure 4 are of the APOS reaction solution after modification of the LD hulls. Absorbance in the 200-400 nm UV region is high, and several dilutions of the sample were required to reduce the absorbance to less than one. While sodium hydroxide and hydrogen peroxide absorb at 201 nm[27] and 210 nm,[28] respectively. Absorbance at wavelengths

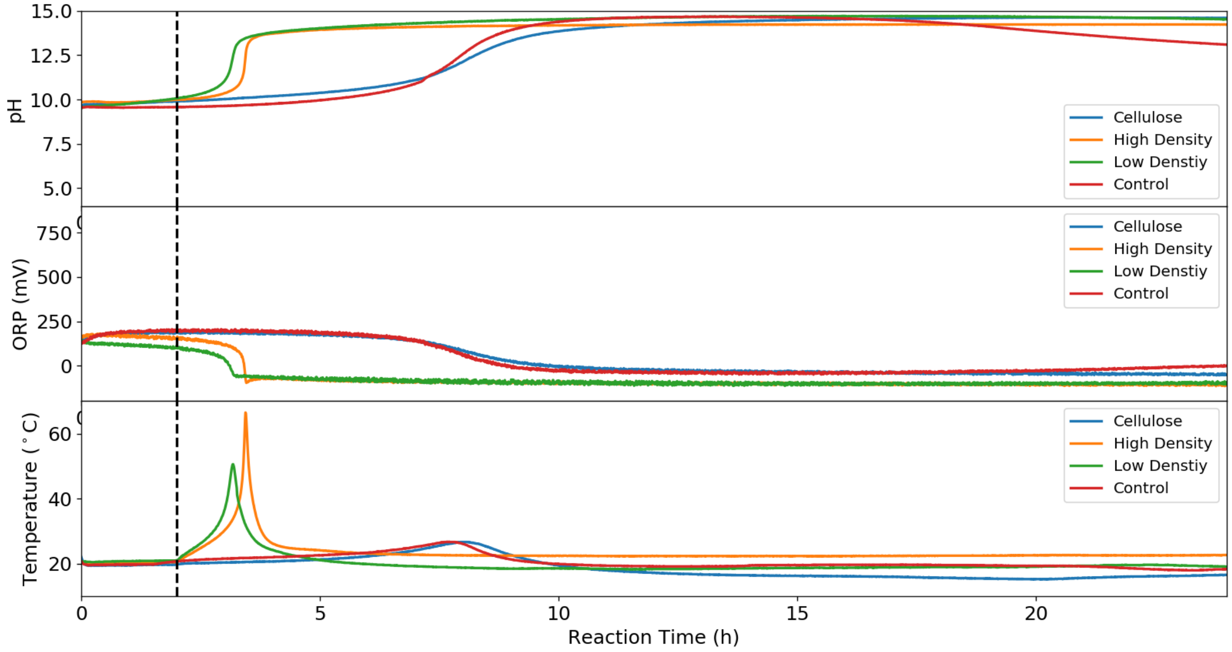

Figure 3. Temperature, oxidation-reduction potential and pH of APOS modifications with high and low density hulls, cellulose, and control. Temperature was held at 20 °C for the first two hours. The dashed line shown is at the 2 h mark when the temperature control was removed.

higher than this are indicative of the presence of conjugated structures. For example, coniferyl alcohol, one of the monomers of lignin, absorbs at 270 nm,[29] while native lignin from hemlock trees has compounds with absorbances at 250 nm, 300 nm, 350 nm in base. The presence of aromatic species in the reaction mixture suggest that components from the hulls are dissolving.

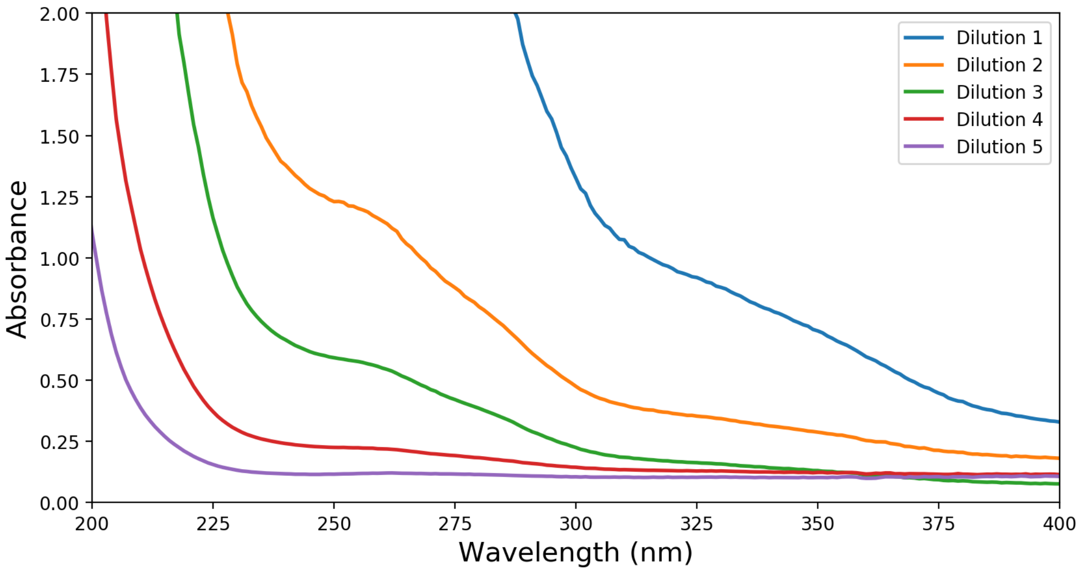

Figure 4. Absorbance spectra of APOS solution after modifying low density hulls.

The decrease in the ORP (Figure 3) indicates that change from an oxidizing environment to a reducing environment. However, the decrease is approximately the same in both the presence and absence of hull material and cellulose. This consistency supports the claim that any change may be due to the interaction between hydrogen peroxide and sodium hydroxide reagents rather than oxidation of the hulls or cellulose. The decomposition of hydrogen peroxide produces water and oxygen:

$$\mathrm{H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g)} \tag{1}$$

After conversion of hydrogen peroxide to the hydroperoxide anion[24,25]

$$H_2O_2 \longrightarrow HO_2{}^- + H^+ \tag{2}$$

the half reactions for the decomposition in base can be written with their known standard potentials:[30]

$$\begin{array}{lll} \text{Reduction:} & HO_2{}^- + H_2O + 2e^- \longrightarrow 3OH^- & E^o = 0.878\text{ V} \\ \text{Oxidation:} & H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2\,e^- & E^o = 0.146\text{ V} \end{array}$$

The overall potential is the sum of the standard potentials, or 1.024 V. This positive value indicates that the decomposition of hydrogen peroxide under basic conditions is a spontaneous reaction which would result in a measured decrease in ORP.

The infrared spectra in Figure 5 of cellulose before and after modification are generally consistent which also supports the idea that the APOS does not modify cellulose. There is a broad shoulder at 1730 cm^{-1} in both high density and low density unmodified hull spectra that disappears upon modification. The disappearance of this band may be due to the conversion of carboxylic acid groups to carboxylate groups, since the reaction takes place in a strongly basic solution.[5,9,31] There is a corresponding increase in the absorbance around 1600 cm^{-1}, which can be attributed to the asymmetric stretch of the COO^-.[4] After soaking the modified hulls in pH 4 buffer, the band at 1730 cm^{-1} does return in the APOS-modified hulls, suggesting the change in hulls was reversible and due to change in the pH rather than oxidation. However, the reappearing band is not as intense. Which may mean that this band in unmodified hulls is from an alkaline soluble component that is being dissolved into basic solution.[5,12] However, an infrared spectrum of the reaction solution did not show a band at this wavenumber.

Potassium Permanganate

Hulls and cellulose were mixed with room temperature 0.01 M potassium permanganate ($KMnO_4$) solution. For comparison, a control reaction was also carried out in which no hulls or cellulose

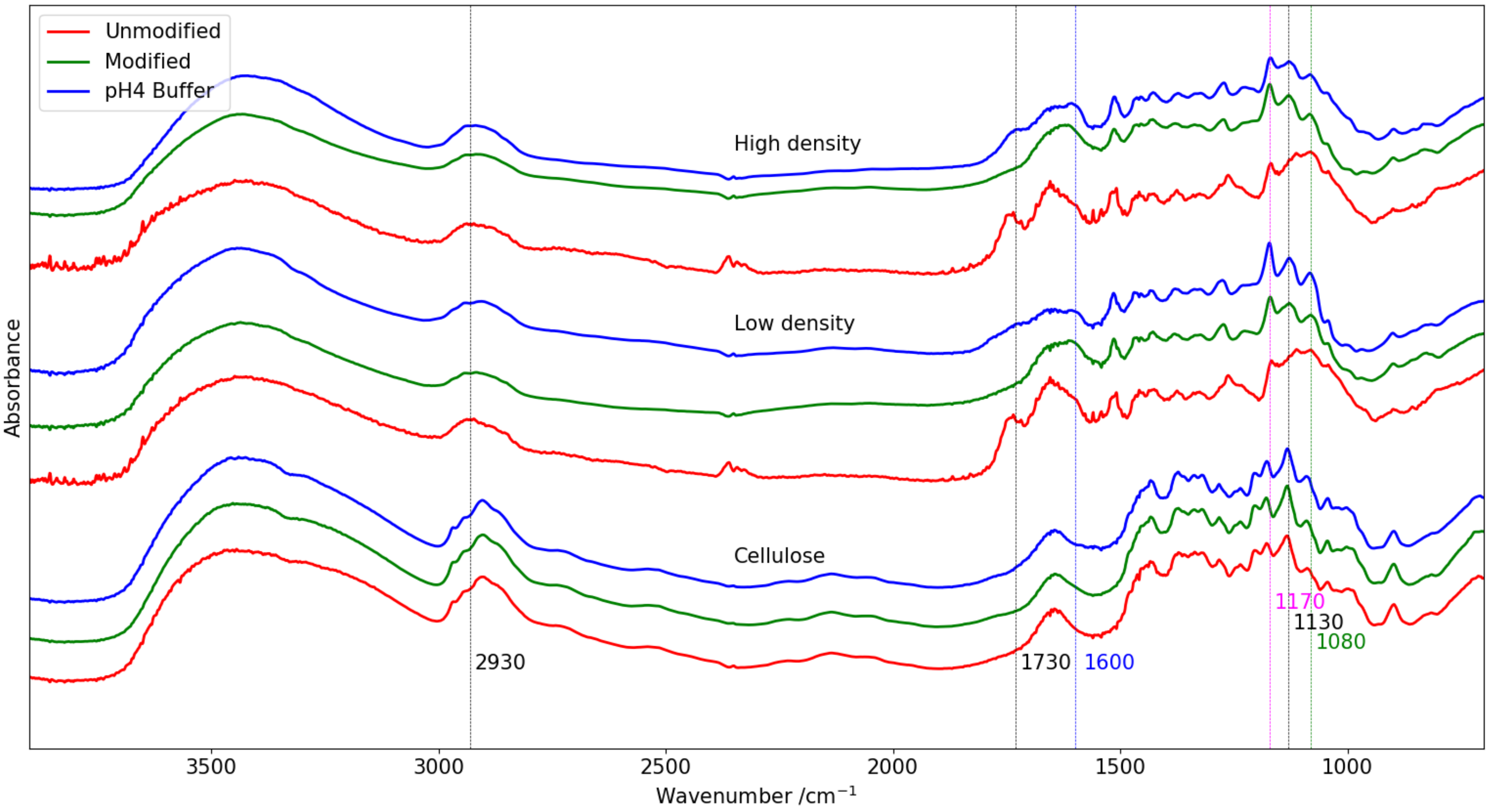

Figure 5. Infrared spectra of unmodified and APOS modified HD hulls, LD hulls, and cellulose. Dashed lines indicate bands of interest labeled with their respective wavenumber in units of cm^{-1}.

were present. For all reactions, there was no observable change in temperature for $KMnO_4$ modifications and the fluctuations shown in Figure 6 are due to fluctuations in ambient temperature. Figure 6 shows that except for a small change at the beginning of the experiment, the control reaction and cellulose reaction again have similar ORP profiles. This suggests that cellulose is not oxidized during the reaction. However, there is a drop in the ORP for the LD and HD hulls (approximately 350 mV and 180 mV, respectively) and a corresponding increase in pH (approximately 1.1 and 1 pH units, respectively), indicating the hulls may have been oxidized by the $KMnO_4$. The change in pH could be attributed to oxidaiton of double bonds as described in the introduction. The change in ORP and pH was delayed by about 3 h and 12 h, respectively, for LD and HD hulls, which could not be explained. Overall, the changes were larger for LD hulls that HD hulls, which could indicate that there is a greater concentration of oxidizable functional groups present in the LD hulls than in the HD hulls. This would make sense if the reaction takes place on the surface of the hulls since LD hulls have a greater surface area to volume ration than HD hulls.[12]

Further evidence of the oxidation lies in the black coating of the hulls. As described previously, this coating is attributed to manganese (II) oxide or manganese (IV) oxide. Both of these compounds are potential products that stem from the reduction of the permanganate ion under basic conditions. These reactions are listed here with their standard reduction potentials:[30]

$$\mathrm{MnO_4}^- + 2\mathrm{H_2O} + 3\mathrm{e}^- \longrightarrow \mathrm{MnO_2} + 4\mathrm{OH}^- \quad E^o = 0.595\ \mathrm{V}$$

$$\mathrm{MnO_4}^- + 3\mathrm{H_2O} + 5\mathrm{e}^- \longrightarrow \mathrm{MnO} + 6\mathrm{OH}^- \quad E^o = 0.34\ \mathrm{V}$$

Other possible reduction products that would result in a black coating of the hulls include Mn_2O_3, $Mn(OH)_2$, and $Mn(OH)_3$, but further speciation of the coating was not attempted. Since the potential for the corresponding oxidation of alcohols groups in the hulls is on the order of 2.5 V,[32] the overall positive potential suggests the oxidation of the hull material would be spontaneous. The greater change in ORP/pH for LD hulls is consistent with the greater surface area to volume ratio of LD hulls determined previously.[12]

Inspection of the infrared spectra of the $KMnO_4$ modified materials in Figure 7 shows that the band at 1650 cm^{-1} appears to gain a small shoulder at 1600 cm^{-1} in all materials modified by $KMnO_4$, with the hulls having the greatest increase in absorbance. As observed with the APOS-modified hulls, this shoulder is consistent with carboxylate formation under basic conditions. Overall, changes in the spectra are small, which may be because the oxidation only occurs on the hull surface. A more significant change imay have been detectable if a different spectroscopic technique were used, such as attenuated total reflection, which is more sensitive to surface changes.

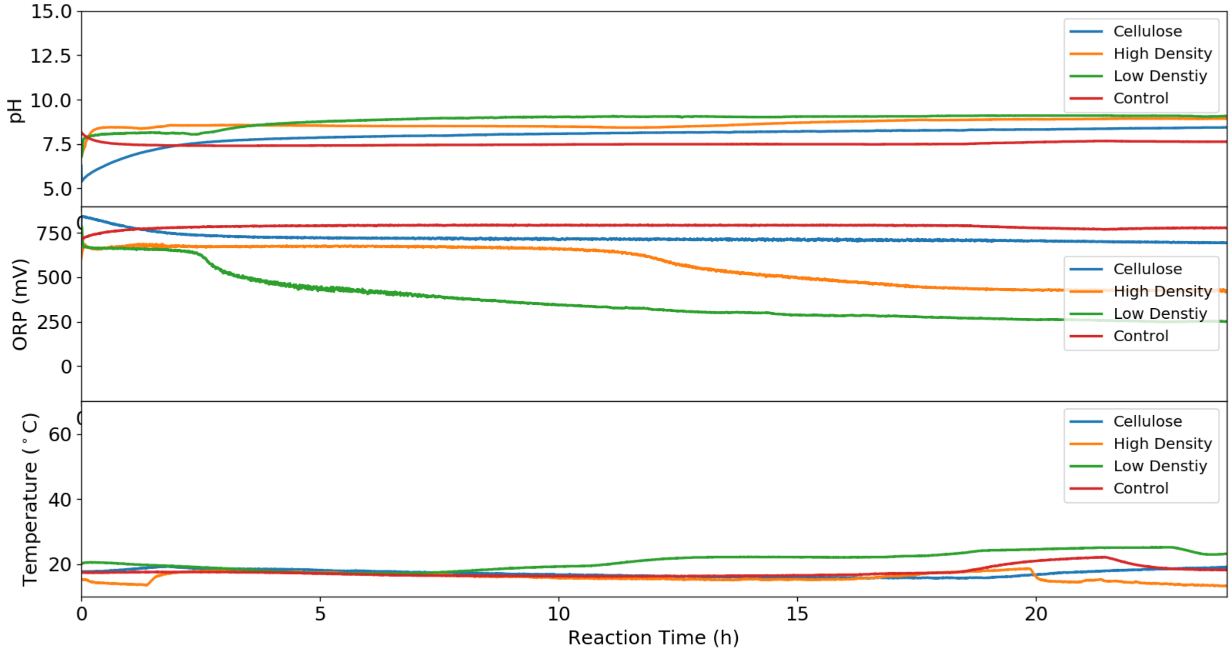

Figure 6. Temperature, oxidation-reduction potential and pH of $KMnO_4$ modifications with high and low density hulls, cellulose, and control. Temperature was allowed to fluctuate normally throughout experiment.

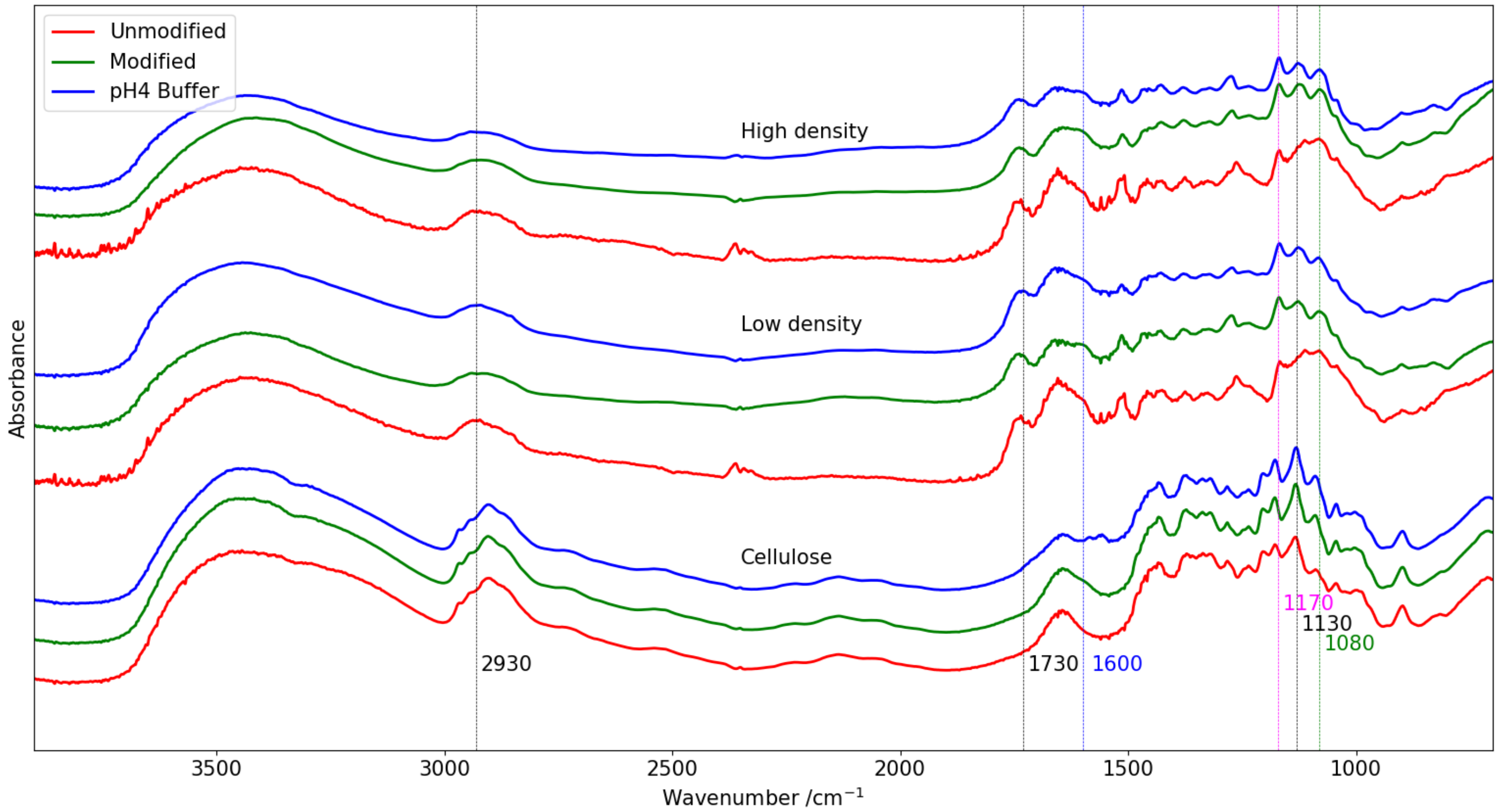

Figure 7. Infrared spectra of unmodified and $KMnO_4$ modified HD hulls, LD hulls, and cellulose. Dashed lines indicate bands of interest labeled with their respective wavenumber in units of cm^{-1}.

Selective Oxidation

The compound (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was used to prepare the TEMPO selective oxidation system (TSOS). Reactions with hulls and cellulose were carried out at room temperature. The pH for LD hull and HD hull reactions were adjusted within the first 15 min of the reaction and the pH for the LD hull reaction was adjusted once again after 23 h to keep the pH around 11, which is optimal for the TEMPO reagent to perform its selective oxidation.[6] For comparison, a control reaction was also carried out in which no hulls or cellulose were present. The control and cellulose were allowed to remain at their starting pH and react uncontrolled. The pH, temperature and ORP were monitored during the reaction an the results are shown in Figure 8. The temperature for all modifications fluctuated with the ambient temperature. With the exception of the HD hull reaction, all reactions showed a decrease in pH by about one unit. However, since this same change in pH is observed in the control, the decrease does not necessarily indicate that a chemical reaction took place in the hulls or the cellulose. The LD hulls and HD hulls reactions show a sharp decrease in ORP within the first 2 h, but the LD hulls reaction ORP begins to increase starting at 5 h suggesting that there is different chemistry happening between the two hull types. The cellulose and control have a similar decrease in their ORP which supports that cellulose is not oxidized by the TSOS. However, other components contained within the hulls may be reacting with TSOS.

Figure 9 shows the infrared spectra of the hulls and cellulose before and after modification. With the exception of the slight increase in intensity in the band at 1170 $\mathrm{cm}^{-1}$for the LD and HD hulls. The spectra do not show significant changes when the hulls or cellulsoe are reactied witht the TSOS, suffesting that either no oxidation occurs or that no chemical reaction can be detected by these methods. However, the small change at 1170 cm^{-1} may indicate a reaction involving either the ether linkages in the glucose backbone or cellulose or alcohols within the hulls.[33]

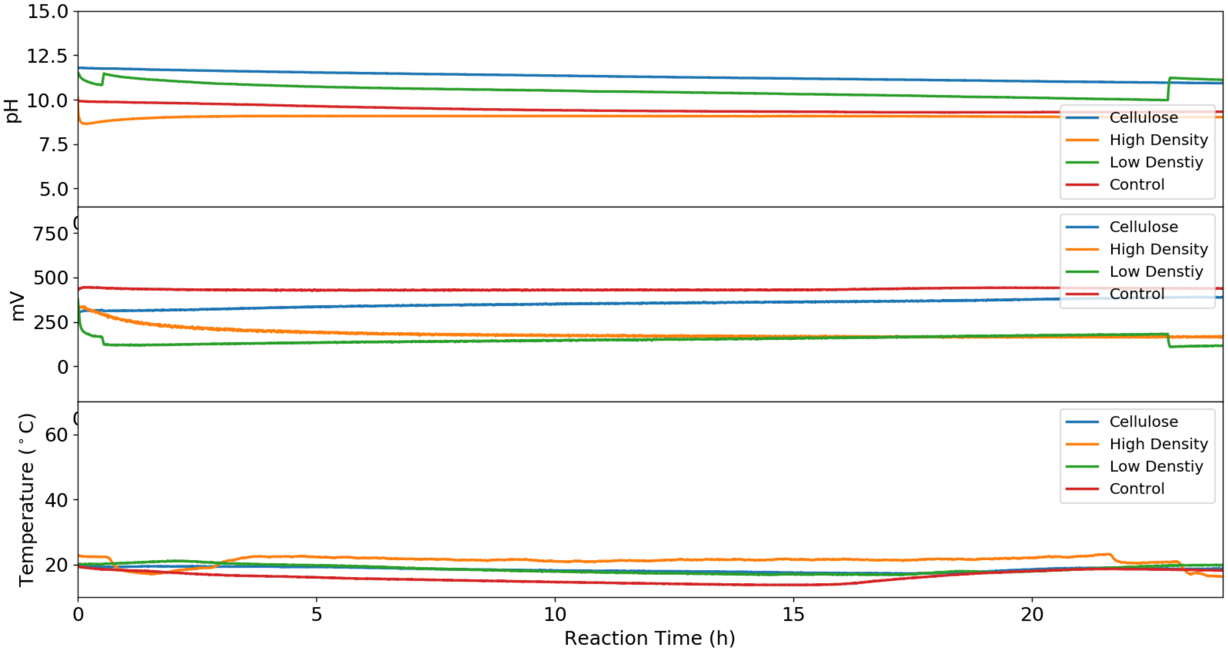

Figure 8. Temperature, oxidation-reduction potential and pH of TSOS modifications with high and low density hulls, cellulose, and control.

Comparison of Oxidation Methods

Infrared spectra for cellulose, LD hulls and HD hulls modified by the different oxidation methods are shown in Figures 10, 11, and 12. For cellulose (Figure 10), with the exception of a small should that appears around 1600 cm^{-1} in the APOS modification, the spectra are virtually identical. This suggests that the reactions did not oxidize cellulose. This result was surprising since the structure of cellulose is well known and the molecule contains oxidizable primary alcohols. One possible explanation is that oxidation occurred but was not detectable microspectroscopic methods employed here. However, changes in pH, temperature, and ORP were consistent with controls, which lends evidence to a lack of oxidation. Another possibility is that crystalline cellulose is resistant to modification, whereas the cellulose from wood pulp more readily undergoes oxidation.[6,15]

For LD and HD hulls (Figures 11) and 12, the most obvious change in the IR spectrum is the

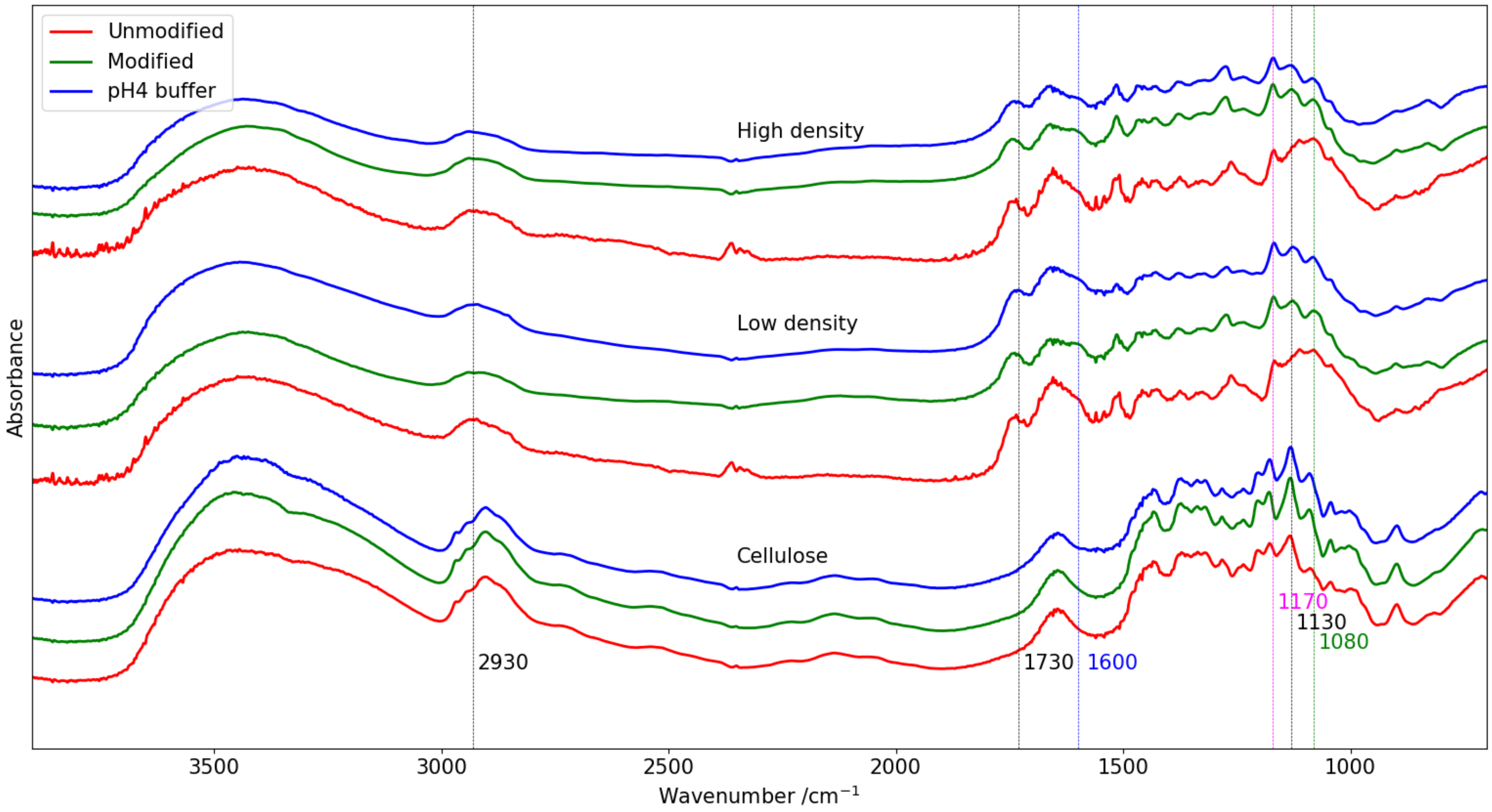

Figure 9. Infrared spectra of unmodified and TSOS modified HD hulls, LD hulls, and cellulose. Dashed lines indicate bands of interest labeled with their respective wavenumber in units of cm^{-1}.

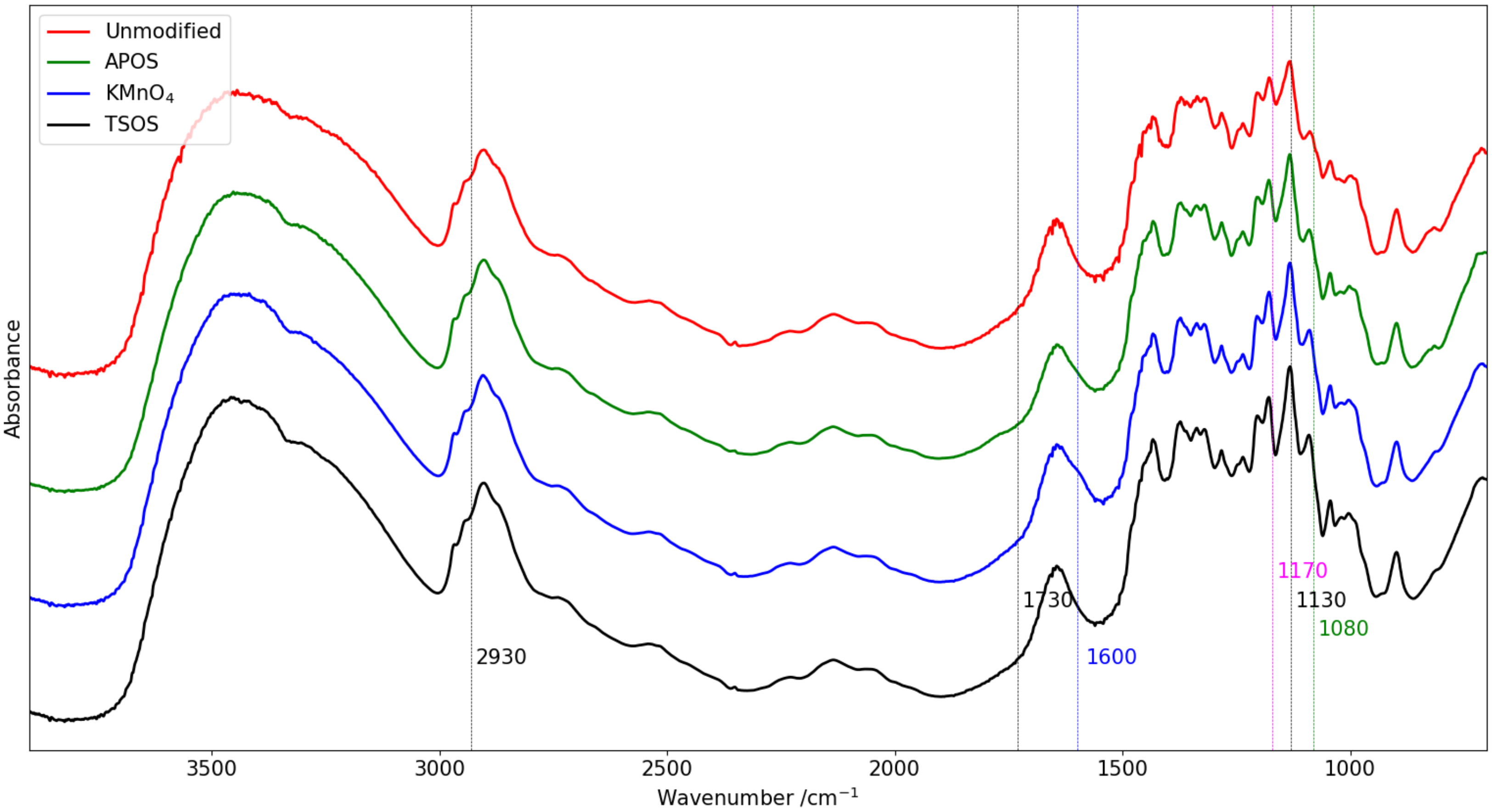

Figure 10. Infrared spectra of all cellulose modifications. Dashed lines indicate bands of interest labeled with their respective wavenumber in units of cm^{-1}.

disappearance of the band at 1730 cm^{-1} when the hulls are modified with the APOS. This change is likely due to the basic conditions converting carboxylic acids to carboxylate groups since a shoulder around 1600 cm^{-1} appears. Lastly, the TSOS reaction did not result in detectable changes in the IR spectra.

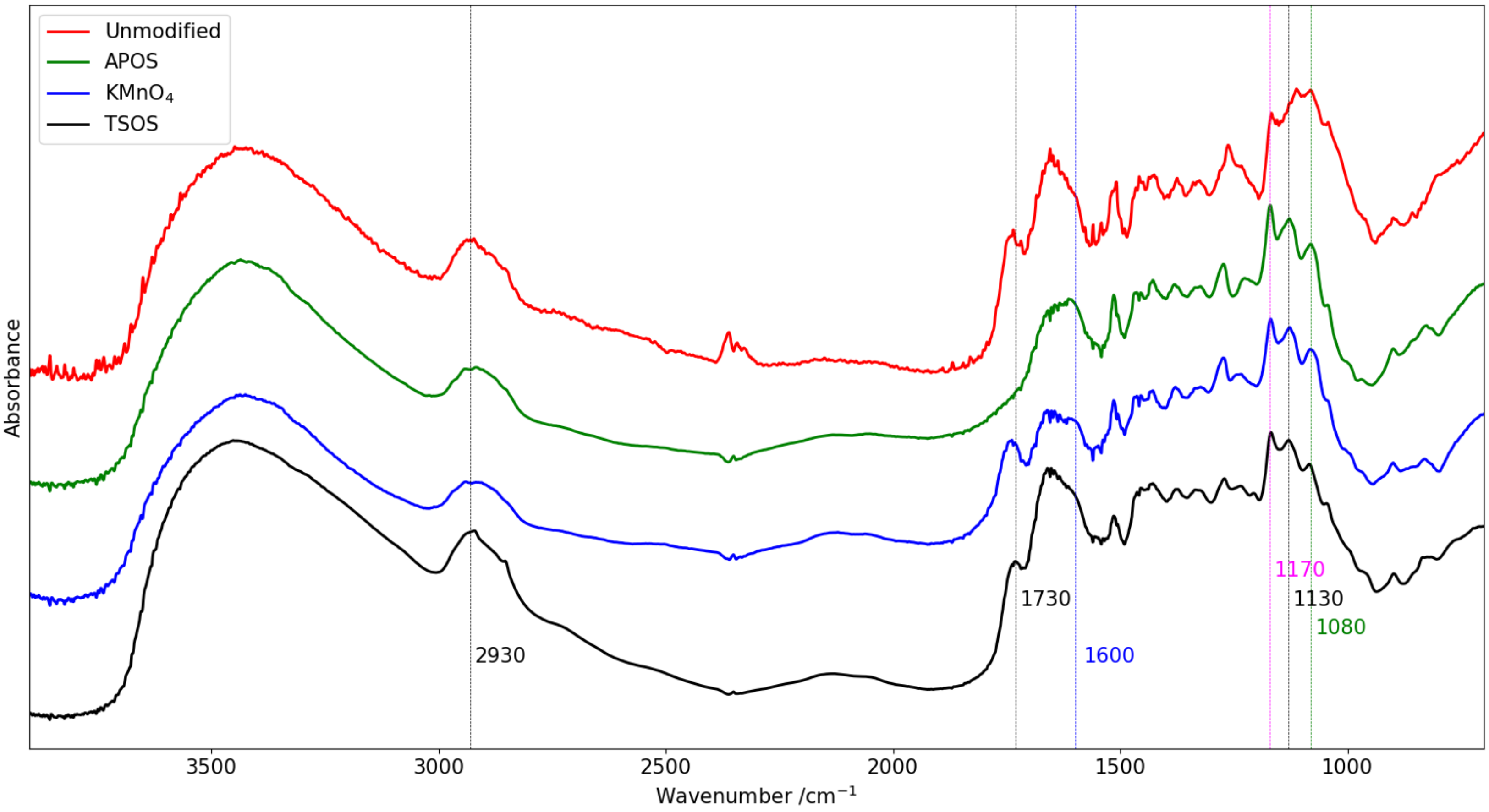

Figure 11. Infrared spectra of all LD hulls modifications. Dashed lines indicate bands of interest labeled with their respective wavenumber in units of cm^{-1}.

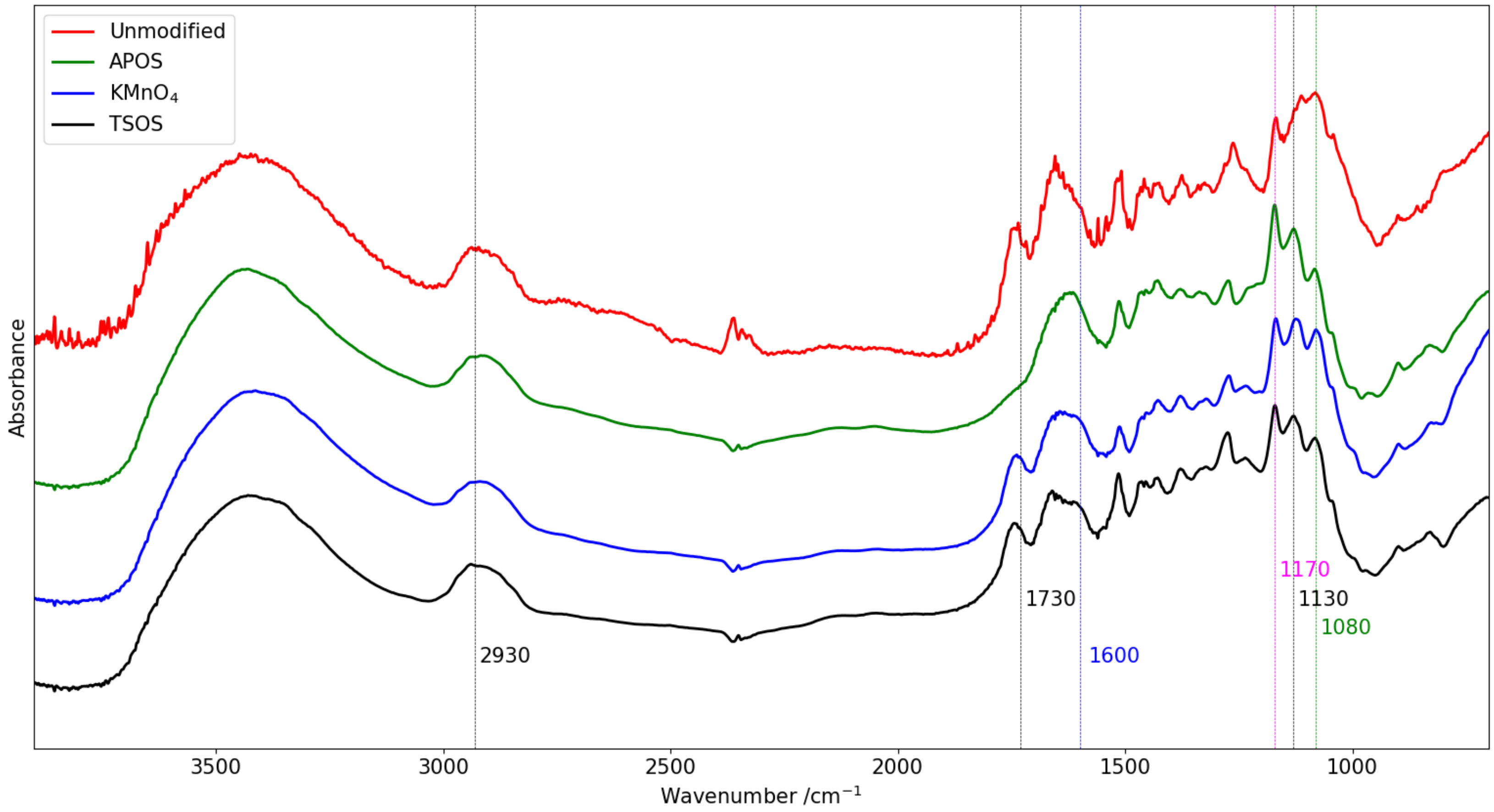

Figure 12. Infrared spectra of all HD hulls modifications. Dashed lines indicate bands of interest labeled with their respective wavenumber in units of cm^{-1}.

CHAPTER FOUR: CONCLUSIONS AND FUTURE DIRECTIONS

Previous studies [11,12,31] have shown that reactions with alkaline peroxide solution result in hulls that have increased uptake in heavy metals and are therefore suitable for biosorption applications. A better understanding of this chemical modification could drive optimization of metal adsorption by hulls. Several oxidation procedures were tested on peanut hulls to determine if they can be chemically modified. These included an alkaline peroxide oxidation system (APOS), a strong oxidizer ($KMnO_4$) and a TEMPO selective oxidation system (TSOS). Reactions with cellulose were also done to determine if any changes to hulls could be attributed to the cellulose content. It was found that the APOS dissolves some components of the hulls into the solution, and increased adsorption capacity is attributable to the resulting increase in surface area rather than oxidized functional groups that may have an increased affinity for metal ions. The $KMnO_4$ likely oxidized the surface of the hulls, as evidenced by the Mn-containing coating on the hulls, but oxidized functional groups could not be detected by infrared spectroscopy. Finally, the selective oxidation method may be oxidizing hull materials, given slight changes in oxidation-reduction potential and pH, but changes in the infrared spectra were subtle and results were deemed inconclusive.

The inability of any of these systems to oxidize cellulose was most surprising since the structure is well known and the molecule contains many oxidizable primary alcohol groups. Future experiments could include a control study with a simpler molecule with a quantifiable number of alcohol groups. A good candidate is octanol since it only has a single primary alcohol group, yet it is insoluble in water, so heterogeneous reaction conditions of the cellulose or hull mixtures could be reproduced. A second improvement to the experiment design would be to use attenuated total reflection infrared spectroscopy to explore changes in the resulting materials. This technique is somewhat surface specific. As such, it would be more sensitive to chemical changes if they are limited to the material’s surface.

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