# Course Syllabus

## PSE 332 – Wood, Pulping and Bleaching Chemistry

**SPRING 2018**

**3 Credit Hours**

### Course Description

The fundamental chemistry of the various wood components will be described together with pertinent information that relates to their industrial processing. Emphasis will be given to the underlying scientific issues that determine the chemistry of the various pulping and bleaching operations. Aspects of environmental accountability as it relates to the pulp and paper industry will also be discussed

### Course Learning Outcomes

Upon successful completion of this course, students should be able to:

* Have an appreciation for the fundamental science that is behind our industry
* To create connections for our industry’s choices
* To create connections that pertain to environmental accountability
* To create a keen interest to students as to the science upon which the technology of the pulp & paper industry rests

# Course Deliverables

Upon completion of the course the student will be able to:

## Describe fundamental aspects of the chemistry of the major wood components; Carbohydrates, Cellulose, Hemicelluloses and Lignin

## Understand the underlying Structural, Polymer and Organic Chemical principles that define their reactivity.

## Describe the chemistry of the main wood components during processing; Pulping & Bleaching

## Become aware of modern developments in wood chemistry & technology

## Be aware of the factors that affect our decisions toward implementing the various technologies and chemicals

## Identify the underlying fundamental scientific principles that ultimately define the engineering decisions toward designing our processes.

### Course Structure

This is a lecture and quiz intensive course. The classes will be video recorded for the benefit of the students to revise the material at will. The process is designed to let students understand and strengthen the information learned and make connections with the industrial processes used in the pulp and paper industry.

### Instructor

**Dr. Dimitris Argyropoulos** (Dr A) - *Instructor*
**Email:** dsargyro@ncsu.edu
**Phone:** 919-515-7708
**Fax:** 919-515-6302
**Office Location:** Biltmore Hall (Robertson Wing) Room 3104
**Office Hours:** by Appointment via e mail or in person consultation,

### Course Meetings

#### Lecture

**Days:** Tuesday, Thursday
**Time:** 11:45am - 1:00pm
**Campus:** Main
**Location:** Lecture Class in Pulp & Paper Building
*This meeting is required.*

### Course Materials

#### Textbooks

**Wood, Pulping and Bleaching Chemistry** - *Argyropoulos, D, S.*  **Course Pack**
**Approximate Cost:** $30-40

*This Course Pack is required.*

#### Expenses

None.

### Requisites and Restrictions

#### Prerequisites[*CH 221*](http://catalog.ncsu.edu/search/?P=CH%20221)/225 and[*CH 222*](http://catalog.ncsu.edu/search/?P=CH%20222)/226 and[*CH 223*](http://catalog.ncsu.edu/search/?P=CH%20223)/227 and[*CH 224*](http://catalog.ncsu.edu/search/?P=CH%20224)/228.Co-requisites

#### Restrictions

None.

### General Education Program (GEP) Information

#### GEP Category

This course does not fulfill a General Education Program category.

#### GEP Co-requisites

This course does not fulfill a General Education Program co-requisite.

### Transportation

This course will not require students to provide their own transportation. For field trips or site visits, transportation will be provided.

### Safety & Risk Assumptions

Not Applicable

### Grading

## GRADING: Class Tests (X10) 50%

 Best 8 will be selected

##  Homework Assignments 20%

##  Final exam 30%

##

**Important Grading Notes**

1. Students in PSE must pass PSE 332 with a grade of C- or better in order to receive credit for the course and move forward in the curriculum.

#### Letter Grades

**This Course uses Standard NCSU Letter Grading:**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 97 | ≤ | **A+** | ≤ | 100 |  |  |  |  |  |
| 93 | ≤ | **A** | < | 97 |  |  |  |  |  |
| 90 | ≤ | **A-** | < | 93 |  |  |  |  |  |
| 87 | ≤ | **B+** | < | 90 |  |  |  |  |  |
| 83 | ≤ | **B** | < | 87 |  |  |  |  |  |
| 80 | ≤ | **B-** | < | 83 |  |  |  |  |  |
| 77 | ≤ | **C+** | < | 80 |  |  |  |  |  |
| 73 | ≤ | **C** | < | 77 |  |  |  |  |  |
| 70 | ≤ | **C-** | < | 73 |  |  |  |  |  |
| 67 | ≤ | **D+** | < | 70 |  |  |  |  |  |
| 63 | ≤ | **D** | < | 67 |  |  |  |  |  |
| 60 | ≤ | **D-** | < | 63 |  |  |  |  |  |
| 0 | ≤ | **F** | < | 60 |  |  |  |  |  |

#### Requirements for Credit-Only (S/U) Grading

In order to receive a grade of S, students are required to take all exams and quizzes, complete all assignments, and earn a grade of C- or better. Conversion from letter grading to credit only (S/U) grading is subject to university deadlines. Refer to the Registration and Records calendar for deadlines related to grading. For more details refer to <http://www.ncsu.edu/policies/academic_affairs/courses_undergrad/REG02.20.15.php>.

For PSE majors, this course must be taken for a grade to count towards the degree.

#### Requirements for Auditors (AU)

Audits of PSE 332 are generally not permitted and must be approved by Dr. Argyropoulos . When approved, students must adhere to the university policy on audits, which may be found at the following link: <http://policies.ncsu.edu/regulation/reg-02-20-04> .

#### Policies on Incomplete Grades

Incomplete (IN) final grades will generally NOT be given for the course, except under unusual circumstances. If an Incomplete is permitted, then Dr. Argyropoulos will give the student a deadline by which the IN must be resolved – usually by the fourth week of the subsequent semester. If a deadline is not authorized by the instructor or department, an unfinished incomplete grade will automatically change to an F after either (a) the end of the next regular semester in which the student is enrolled (not including summer sessions), or (b) by the end of 12 months if the student is not enrolled, whichever is shorter. Incompletes that change to F will count as an attempted course on transcripts. The burden of fulfilling an incomplete grade is the responsibility of the student. The university policy on incomplete grades is located at the following link: [http://policies.ncsu.edu/regulation/reg-02-50-03](http://policies.ncsu.edu/regulation/reg-02-50-03%20) .

#### Late Assignments

Assignments turned in after the specified time may or may not be accepted by the instructor, and they may be subject to grade penalties.

### Attendance Policy

#### Attendance

It is not expected that any student can do well in PSE 332 (or even pass the course) without regular class attendance. A roll will be passed out in random class sessions. Quizzes and homework missed during an unexcused absence can NOT be made up.

Excused absences are accepted only for cases of emergency, documented illness or incapacitation, or extenuating circumstances as described by the NCSU policy detailed at the following link: [http://policies.ncsu.edu/regulation/reg-02-20-03](http://policies.ncsu.edu/regulation/reg-02-20-03%20) .

Any excused absence requires that the student provide adequate written documentation by the start of the first class period following the period of absence. Students are expected to make up all work missed during the excused absence period.

### Academic Integrity

#### Academic Integrity

Students are required to comply with the university policy on academic integrity found in the Code of Student Conduct found at

<http://policies.ncsu.edu/policy/pol-11-35-01>

All work (quizzes, tests, projects, homework, etc.) will be conducted in accordance with the Code of Student Conduct.

Any students caught cheating or plagiarizing or helping others to do so will be subject to disciplinary action, including failing of the course and referral to the NCSU judicial system. It is understood that the student’s signature on any test or assignment means that the student neither gave nor received unauthorized aid. ***Taking the weekly quizzes while in the presence of or in communication with another student in the course will be considered cheating.***

#### Academic Honesty

See <http://policies.ncsu.edu/policy/pol-11-35-01> (Section 8) for a detailed explanation of academic honesty/dishonesty.

#### Honor Pledge

Your signature or printed name on any test or assignment indicates "I have neither given nor received unauthorized aid on this test or assignment."

### Electronically- or Web-based Course Components

1. E-mail -- This course will rely heavily on the use of students’ Unity e-mail accounts. General notices, assignments, and other course activities will be transmitted through these e-mail accounts. Students are responsible for a) checking their account each day for course announcements or other activities; and b) keeping their account current (e.g. not filled up) so that it can receive messages from the instructor. Failure to meet course requirements due to failure to meet these e-mail account responsibilities will not be excused.

### Accommodations for Disabilities

Reasonable accommodations will be made for students with verifiable disabilities. In order to take advantage of available accommodations, student must register with the Disability Services Office (<http://www.ncsu.edu/dso>) located at 1900 Student Health Center, Campus Box 7509, 515-7653. For more information on NC State's policy on working with students with disabilities, please see the Academic Accommodations for Students with Disabilities Regulation at <http://policies.ncsu.edu/regulation/reg-04-20-06> .

### Non-Discrimination Policy

NC State University provides equality of opportunity in education and employment for all students and employees. Accordingly, NC State affirms its commitment to maintain a work environment for all employees and an academic environment for all students that is free from all forms of discrimination. Discrimination based on race, color, religion, creed, sex, national origin, age, disability, veteran status, or sexual orientation is a violation of state and federal law and/or NC State University policy and will not be tolerated. Harassment of any person (either in the form of quid pro quo or creation of a hostile environment) based on race, color, religion, creed, sex, national origin, age, disability, veteran status, or sexual orientation also is a violation of state and federal law and/or NC State University policy and will not be tolerated. Retaliation against any person who complains about discrimination is also prohibited. NC State's policies and regulations covering discrimination, harassment, and retaliation may be accessed at [http://policies.ncsu.edu/policy/pol-04-25-05](http://policies.ncsu.edu/policy/pol-04-25-05%20) . Any person who feels that he or she has been the subject of prohibited discrimination, harassment, or retaliation should contact the Office for Equal Opportunity (OEO) at 515-3148.

## Course Schedule

# Week 1, Introduction, Outline & Crash Course In Organic Chemistry, Definitions, Nomenclature

**Week 1** , Ultrastructure of Wood

# Week 2 Chemistry of Carbohydrates, Definitions

# Week 2 Isomerism, Chirality, ConformationsQuiz 1

# Week 3 Carbohydrate Reactivity; Glucosides, Ethers,

# Week 3 Carbohydrate Oxidations, Reductions, Hydrolyses

# Quiz 2

# Week 4 Oligosaccharides; Disaccharides,

# Week 4 Polysaccharides

# Quiz 3

# Week 5 Polymer Chemistry, Fundamentals, Week 5 Structure, Morphology of Cellulose, Hemicelluloses

# Week 6 Lignin Biosynthesis and StructureWeek 6 Lignin Structure continued, New Lignin Structures,

# Quiz 4

# Week 7 Principles of Pulping Chemistry,

# Week 7 Pulping Chemistry, Reactions of Cellulose, Peeling, Stopping,

# Week 8 Reactions of Lignin; Sulfite;

# Week 8 Reactions of Lignin; Soda,Quiz 5

# Week 9 Reactions of Lignin under Kraft Conditions

# Week 9 Condensation Reactions in Lignin Quiz 6

# Week 10 Structure of Kraft Lignin,

# Week 10 Bleaching Chemistry Definitions

# Quiz 7

# Week 11 Chlorine Dioxide Bleaching, Process Details,

**Week 11** Chlorine Bleaching Chemistry

Quiz 8

# Week 12 Oxygen Delignification,

# Week 12 Details of Process Limitations

Quiz 9

## Week 13 Peroxide, Delignification,

**Week 13** Ozone Delignification

Quiz 10

Final exam Date and location set by NCSU

## PAST QUIZZES FOR STUDENT USE & PRACTISE

**QUIZ 1**

1. What is a carbohydrate? What is the general formula? [5 marks ]
2. Write down the Chair configuration of a pyranose sugar (i.e glucose) and [25 marks] :
* Number the different carbons bearing secondary OH’s…………………..
* Number the different carbons bearing primary OH………………………
* Label the Anomeric Carbon …which one it is:?........................................
* How do you Define an axial and an equatorial OH ?.
* Which one is of a higher energy content the axial or the equatorial conformation?

Check the correct one:

1. What is the name of the tissue where wood formation takes place? Where is it located? [10 marks]
2. What is an annual ring made of and why you can actually see it? [10 marks]
3. What are the various layers within a fiber ? Please draw [15 marks]
4. Where most of the lignin in a tree resides? [10 marks]

7. There are two main categories of trees. Please name them. They are composed of a variety of different cell types; In the sections below **briefly** discuss the following terms:

Note: **Key word**s indicating some Technological Ramifications/Connections will be appreciated (20 marks)

Fibres; Libriform;Bordered Pit & Torus membrane; Middle Lamella

8. What is Reaction Wood? Where does it occur and how it differs in softwoods and hardwoods (5 marks)?

**QUIZ 2**

1. During Photosynthesis what is the name of the molecule that initially interacts with sun light?[5 marks]

2. What are the characteristic and functional features of the molecule in Question 1?[15marks] :

3. What is a nucleotide and a nucleoside and how is energy stored in the nucleotides? [5 marks]

4. Given the molecular formula C3H6O please draw two constitutional isomers both containing a carbonyl group (10 marks)

5. What is *chiral* centre *or a stereocentre* ? Give an example [5 marks]

6. How do two enantiomers differ? [5 marks]

7. How does one tell one enantiomer from another? (Keyword will suffice) Please make reference to:

Their interaction with light [7 marks}; The polarimeter [6 marks]; Specific Rotation? [7 marks]

8. What is mutarotation and what does it prove [10 marks]?

9. How do the ring systems of sugar molecules form [10 marks]?

10. Cellulose is sensitive to both acidic and alkaline environments. Please specify the following: a. Which environment is more damaging to cellulose [ 2 marks], b. Why? [10 marks]; C. What commercial implications does this have as far as the Pulp & paper Industry is concerned? [3 marks]

**QUIZ 3**

1. Please describe the products that result from the Periodate (HJO4) oxidation of (5 marks each) :

R

CH

OH

CH2OH

R1

CH

CH

R2

OH

OH

CH

OH

2. What is the utility of reaction of sugars with phenylhydrazine (5 marks)? Please include a reaction scheme (5 marks) and the names of the products (5 marks)

3. Show the overall Peeling (5 marks) and stopping (5 marks) reactions that occur when cellulose is treated with alkali.

4. Under acidic conditions a sugar in the presence of gaseous HCl and methanol is *selectively methylated at the anomeric position,*  Why? Your answer should include: A reaction diagram (5 points); Charge stabilization considerations and movement of electrons (5 points); Why alternative scenaria of methylation would NOT work? (5 points).

What is the name of the structure below and what does it attempt to convey in the light of Acid hydrolysis of the glycosidic bond (5 marks)?



5. A polymer sample consists of 9 molecules of molecular weight 30,000 g/.mole and 5 molecules of molecular weight 50,000 g.mole. Enter these data to the appropriate formulae that describe: ( No need to do proceed with the final calculations)

Please show the notation used for each of these terms (10 marks). ; The Number Average Molecular weight:; The Weight Average Molecular weight:; The Z average Molecular weight:

6. Please define Polydisperisty, using some of the above terms (5 marks)

7. Please draw a typical Molecular weight Distribution curve and approximately allocate the above three averages in it (5 marks).

8. What does the equation below try to convey ? Your answer should include :

Hint : A diagram will be helpful

The name of this equation; Correct spelling NOT essential (5 marks)

Definition and explanation of all the symbols (10 marks):

Using the Data of the Table below and in light of the above equation what can one tell about the macromolecules of Kraft Lignin and Xylan (10 marks)?

(Hint : A diagram will be helpful)



**QUIZ 4**

1. Hemicelluloses make up approximately 1/3 of the chemical composition of hardwoods and softwoods. Name the major hemicelluloses found in Softwoods & Hardwoods(5 marks) ; Draw the structure of the major hemicellulose found in softwoods (Abbreviations for the different sugar units are accepted) (10 marks); indicate the monosaccharide components (*names*) and *type(s) of glycosidic* *linkages* (5 marks)

*Use: abbreviations* ***Glu for Glucose*** *,* ***Man for Mannnose****,* ***Gal. For Galactose****,* ***Xyl. For Xylan****,* ***Arab. ForArabinose***

***2.*** Draw the structure of cellulose and point out its structural features (10 marks) i.e endocyclic oxygen, cellobiose unit, reducing end group, non-reducing end group, type of linkage between units, primary and secondary OH’s

3. Native Cellulose I is considered to be a rigid structure, Why? Your answer should include the types of H- bonding that occur within cellulose (15 marks).

1. The biosynthesis of lignin involves a set of discrete steps.
	1. Describe these steps using only words; Turn the page if you need more room (10 marks)
	2. In the reaction scheme below a serious error exists, please indicate where

the problem is (5 marks)



1. Show how coniferyl alcohol is converted to :
2. A phenoxy free radical (5 marks)
3. A C centered free radical (5 marks
4. Combine steps (i) & (ii) to createthe most abundant -0-4 bond in lignin and explain why this bonding pattern is the most abundant in lignin? (15 marks)
5. Explain the main differences in the lignins of (15 marks) : Annual Plants;. Softwoods;. Hardwoods

**QUIZ 5**

1. During the random dehydrogenative (DHP) polymerization of lignin, amongst others, the following three linking patterns are created: -and'. Show the detailed mechanism of formation for these moieties (15 marks).
2. Early theories regarding lignin structure had a deficiency as far as the nature of the branch point in lignin was concerned. Using one of the structures created in question 1 show how a structure in lignin can be created that may account for the degree of branching usually encountered in it (10 marks).
3. Discuss the technological relevance of the structure created in question 2 to modern pulping and bleaching processes (10 marks). Use a point form to convey your message.
4. In the structure below identify at least five structural features discussed in class.

Use arrows to indicate your answers (10 marks).

5. During pulping the various wood components are dissolved in a manner shown in the graph below. Discuss the reasoning why xylan does not dissolve away as rapidly as Glucomannan. Your answer should include a reaction mechanism that justifies this (15 marks). Also discuss what reactions are taking place in cellulose making susceptible to yield losses at temperatures above 170 0C (15 marks).



6 . During the early stages of pulping lignin is liberated in fragments that are of progressively increasing molecular weight. The Gel Degradation Theory can account for these observations. Describe this theory using a diagram and appropriate notes on it (15 marks).

1. Indicate two reactions which consume alkali during pulping (5 marks). What consequence these may have in terms of pulping effectiveness? (5marks)

**QUIZ 6**

1. Identify and Draw the most significant transient structure that occurs within lignin during alkaline pulping ( 5 marks). Show the detailed mechanism of its formation from β-O-4 ether moieties (15 marks).
2. Draw the reaction mechanism for the cleavage of non-phenolic β ethers (10 marks). Identify a group within these structures that when present will make these moieties inert toward alkaline pulping (10 marks).
3. Discuss the structures that may form when γ elimination reactions occur during alkaline pulping (10 marks). Please describe the relevance of the formed structures to how they may affect modern pulping and bleaching operations (10 marks). Use a point form to convey your message.
4. Compare and contrast the chemistry of soda and that of kraft pulping. In particular your answer should be focused at the dissociation constants of the resulting species that are created when the respective nucleophiles attack the quinone methide. (20 marks).
5. Show the reaction that describes ; Two condensation reactions that take place during alkaline pulping (10 marks); Describe and discuss a condensation reaction that is less favorably affected by the use of the Extended Modified Chemical Cooking Process, compared to a batch process (10 marks).
6. **QUIZ 7**
7. Define carbohydrates in chemical terms (elemental composition, functional groups) and give examples for **mono-, oligo- and polysaccharides**. **(10 points)**
8. Draw structural segments of **cellulose** and **amylose** in the proper configuration and try to rationalize & explain why amylose is water soluble and cellulose is not. **(10 points).** Draw the various types of H-bonding that occur in cellulose **(5 points)**
9. Draw the monomeric product (and its **resonance forms**) from the reaction of coniferyl alcohol and Peroxidase/H2O2. **(5 points)**



1. From the products formed in problem # 4.

 **Show how** **C5-C5** and **-O-4** dimers are formed. **(10 points)**

 Explain how **lignin-carbohydrate complexes** are formed during lignin formation (HINT: nucleophilic addition to quinone methide intermediates ) **(10 points**

**QUIZ 8**

1. What are the differences between **compression wood** and **tension wood (8 points)** ? What is the **G-layer** and **where is it found**? **(2 points)**
2. The following Figure shows the removal of wood components during a kraft cook of a softwood. Based on your knowledge of the underlying chemistry responsible for the removal of polysaccharides and lignin, discuss the following:

What is the purpose of pulping? (**2 points**); What causes the differences in the removal of xylans & galactoglucomannans. (show the appropriate reaction mechanisms and include structures of the two hemicelluloses) (abbreviations will be accepted) (**13 pts**); Why are the yield losses in cellulose yield limited to about 6-8%? (**5pts**)



1. Please explain why the kraft chemistry is more efficient than the soda chemistry toward wood delignification **(10 marks)**. Do the differences that you are about to describe have an affect in the cleavage of etherified *Beta*-ether units? Yes or No and Why? **(5 marks)**
2. What is the reason for the observed odor associated with Kraft pulping? Name and draw the chemical responsible, as well as a typical reaction leading to their formation **(5 points)**

**QUIZ 9**

1. Why do we bleach pulp? Your answer should include detailed mention of the structures that are present in residual Kraft lignin as opposed to the native lignin in wood. (5 marks).
2. What are the different categories that various bleaching reagents can be classified to?( 5 marks).
3. Indicate the most common chlorine and oxygen based bleaching reagents used by the pulp and paper industry (10 marks).
4. For the two sets of reagents identified in question 3 indicate the active species for each of them and classify them in accordance to the categories you mentioned in question 2 (10 marks)
5. Define and explain the term “OXE”. Your answer should include the equations that determine OXE for the various bleaching reagents (15 marks)
6. Chlorine dioxide operates at an optimum pH of 4.2. Using a graph indicate and explain why (10 marks) .
7. Using a bullet form enumerate the benefits that chlorine dioxide offers in bleaching including the bonus benefits toward cellulose (10 marks)
8. What are the main differences in the mechanism of the reactions of Chlorine Dioxide with lignin phenolic and non-phenolic structures? (5 marks)
9. Despite every effort, ECF bleaching is associated with organochlorine. Indicate the reactions and the species responsible for the formation of chlorine during chlorine dioxide bleaching (10 marks)

**QUIZ 10**

1. Indicate the reasons that occur when oxygen is reduced to water. Your answer should include all electronic steps involved and the species formed. (15 marks).
2. During the four electron reduction of oxygen to water a number of transient species form. For the purposes of understanding the effect of oxygen onto lignin structures we need to classify them into electrophiles and nucleophiles. Please classify them accordingly and indicate the specific parts of the lignin phenyl propanoid that they could attack. Show solid arrows for the main points of attack and broken arrows for the minor points of attack. (20 marks).
3. During oxygen delignification a variety of transient reactive species are created. Indicate which oxygen species react in the mixer and which react in the reactor. (5 marks).
4. Indicate the initial sets of reactions that take place between oxygen and lignin (10 marks). Identify what kind of units in lignin are required to do this (5 marks).
5. During oxygen delignification phenoxyl radicals are created which may react with other reactive oxygen species in several different ways causing ring oppenting products via the formation of activated intermediates