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Light Absorption By Organic Carbon From Wood Combustion

Yanju Chen
Tami C. Bond
Christoph A. Roden
University of Illinois at Urbana- Champaign

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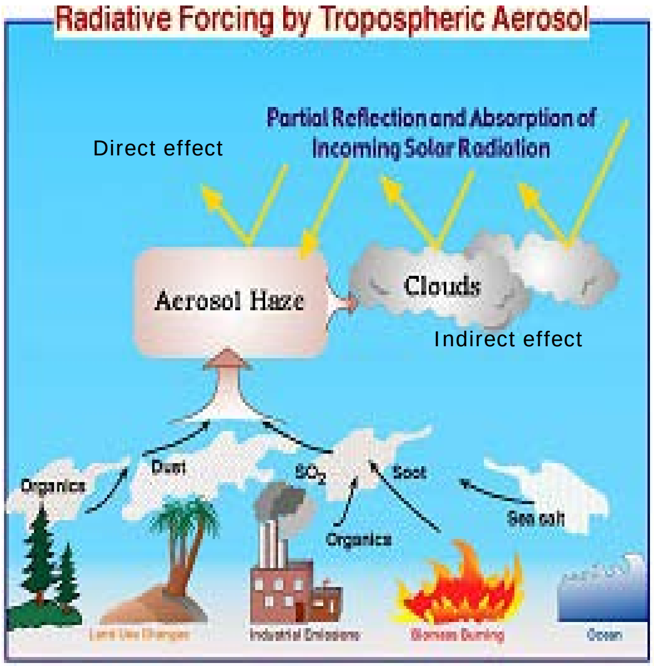
OVERVIEW

- Carbonaceous aerosols are a large fraction of both urban and global aerosol
  - Affect global radiative balance by scattering and absorbing light
  - Impacts on agriculture due to reduced sunlight
  - Effect on reflectivity of clouds



Source: http://www.pmel.noaa.gov/

WHY EXAMINE ABSORPTION BY ORGANIC CARBON

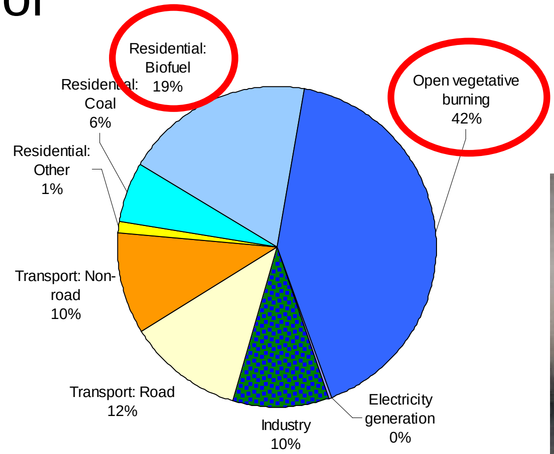
- Carbonaceous aerosol is composed of black carbon (BC) and organic carbon (OC).
- BC is the most absorbing aerosol, *BUT*……
- OC has complex composition, and is estimated to be ten times more abundant than BC (10-70% of total fine aerosol mass)
- OC may also have significant absorption, which is greater at near-ultraviolet and blue wavelength (around 400nm)
- This absorption would affect radiative transfer.
- Evidence for absorbing OC
  - Summarized by *Andrae and Gelencser (2006), Sun et al (2007), and Bergstrom et al. (2007)*
  - Measured by *Bond et al. (2001), Kirchstetter et al. (2004), Roden et al. (2006)*

WHY CHOOSE AEROSOL FROM BIOMASS BURNING

- Biofuels and open vegetative burning contribute a large amount of primary, combustion-related OC (~70%).

- Biofuels: wood, crop residue, charcoal used for heating and cooking

http://www.flickr.com/photos/elmada/253979357/



Source: Bond, Streets et al., JGR 109, D14203, doi:10.

- Open vegetative burning: forests, fields, and savannas

http://www.thewe.cc/weplanet/news/forests/clock_ticking_for_indonesian_rainforest.htm

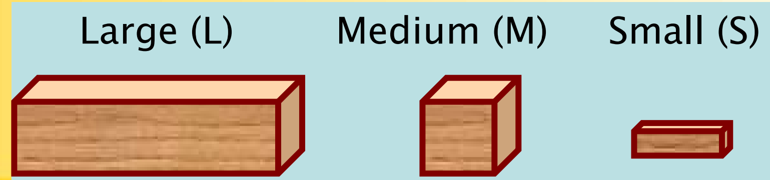
Motivation

- Generation type may affect optical properties of OC (*fuel composition, fuel size, combustion conditions*)
- Field observations:
  - Same fuel → different emission quantities & properties
  - Therefore, *combustion conditions* in addition to fuel composition affect emissions
- Ultimate goal: Parameterize OC emissions in terms of combustion and fuel type

OBJECTIVE

- Isolate **controlling variables** of wood combustion, determine key governing factors to parameterize emission models.
- Provide **optical properties** of organic carbon emitted from wood combustion for use in radiative transfer models.

METHOD

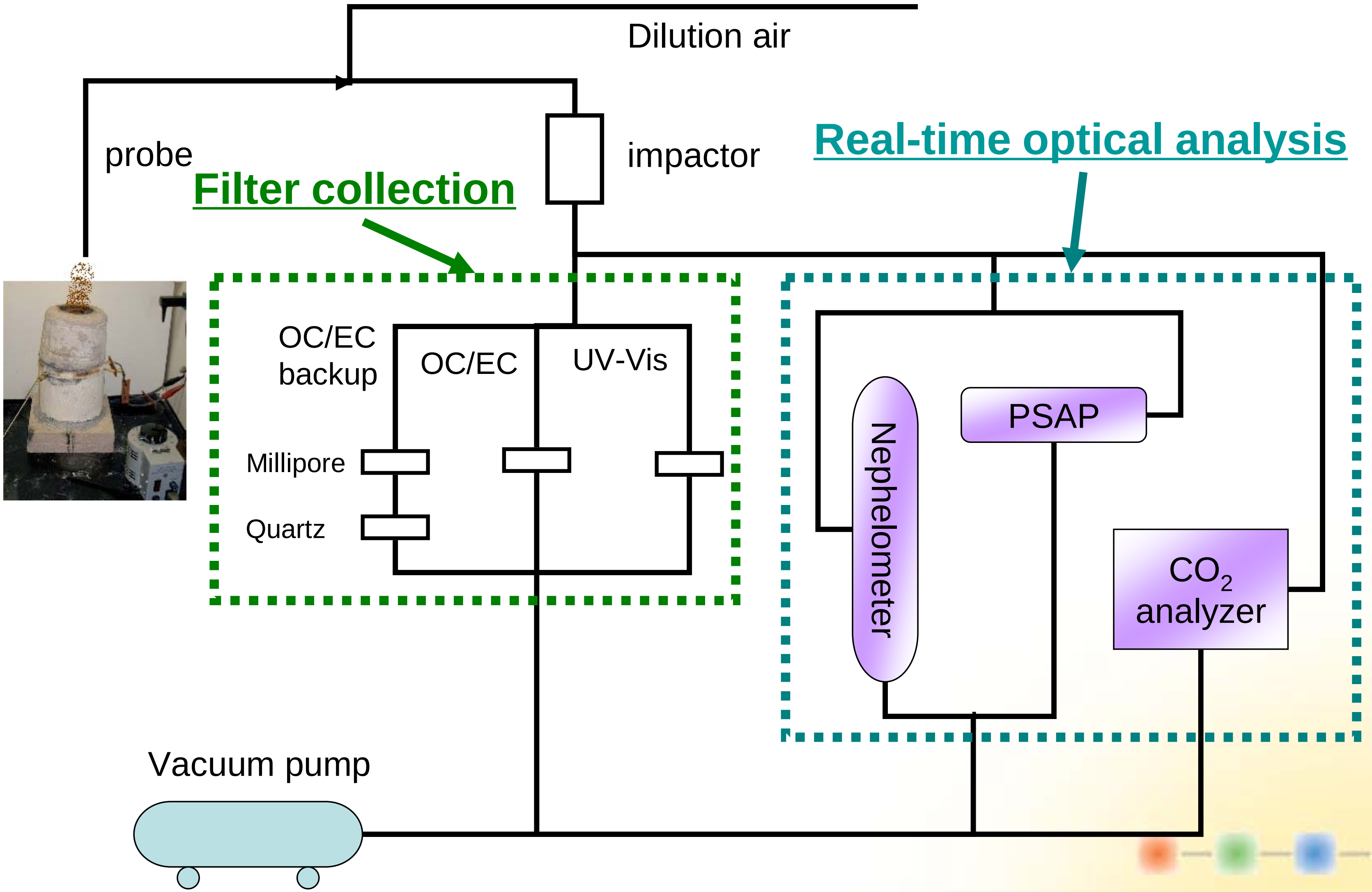


- Generate samples in a laboratory combustor under different conditions

Wood type	Pine, oak
Wood size	3/4”× 1/4”×3/4” (***S***), 3/4”×3/4”×3/4” (***M***), 9/4”×3/4”×3/4” (***L***)
Initial burning temperature	200±5 ℃, 380±5 ℃, 500±5 ℃
Burning condition	Smoldering

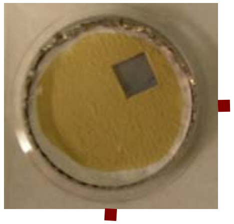
- OC samples were collected on quartz filters for analysis.
- Extraction: polar and non-polar solvents (acetone, methanol, DI water and hexane)
- UV-Vis absorption measurement of extract solutions: Shimadzu UV-2401 UV-Vis recording spectrophotometer
- Total aerosol carbon: Sunset OC/EC analyzer
- Real-time absorption and scattering

SAMPLING SCHEMATIC



EXTRACTION

Quartz filter



A punch of original sample filter analyzed in OC/EC analyzer

Solvents
(acetone, methanol, hexane or DI water)

Sonicate for 1hr

Maintain at room temperature for 19hrs

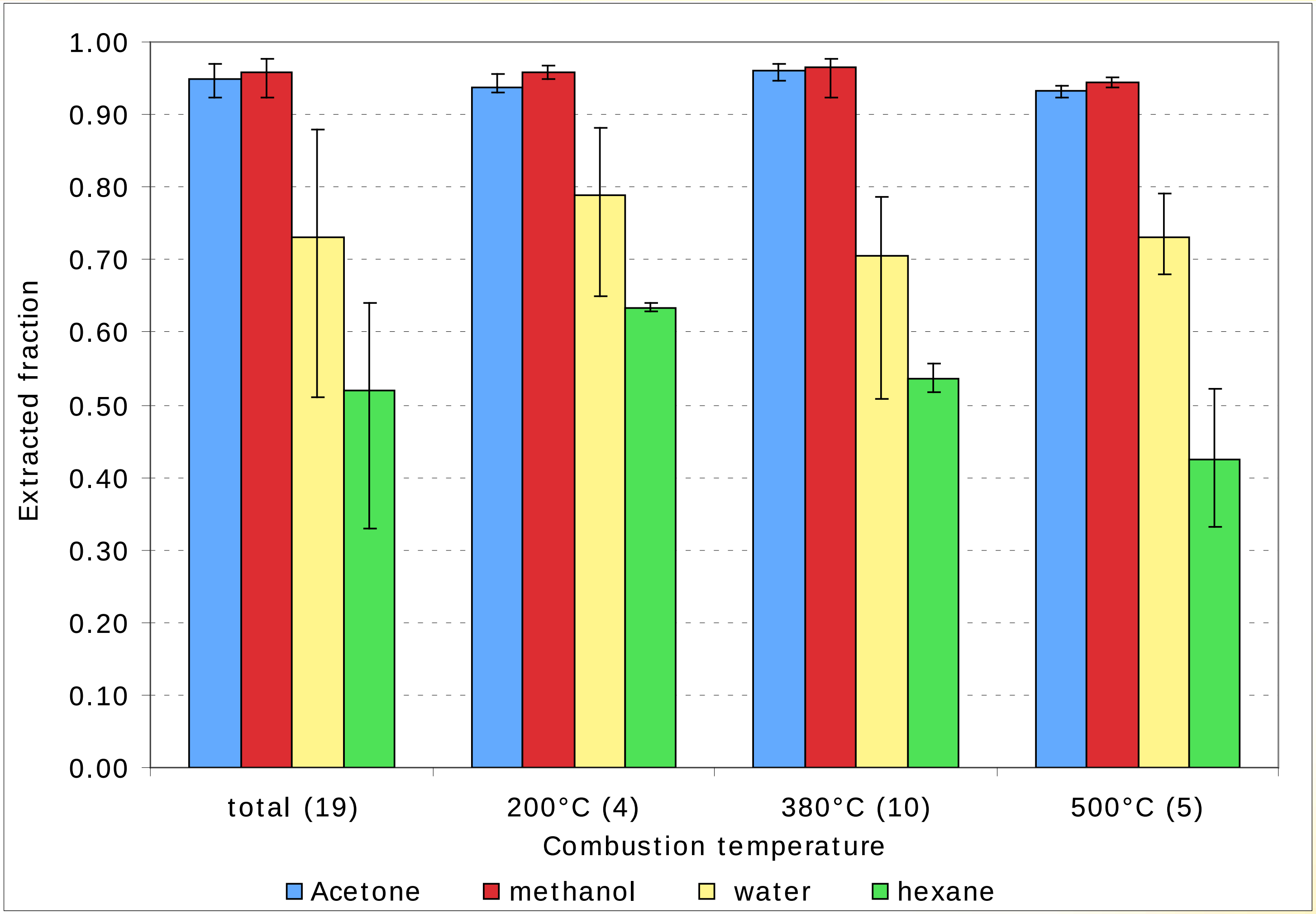
Sonicate for 1hr

filtration

Residual filter after extraction
dried & analyzed in OC/EC analyzer

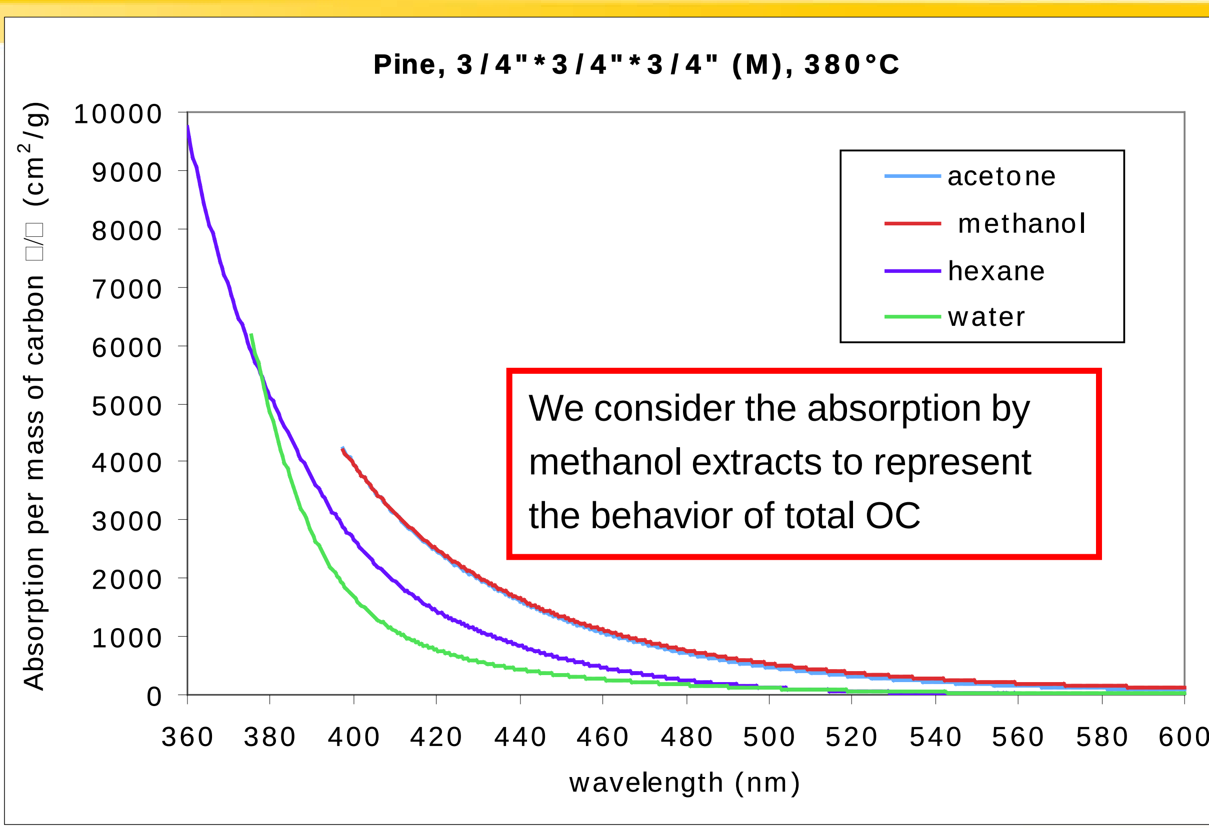
Extract solution
analyzed in UV-vis spectrophotometer

EXTRACTED FRACTIONS



Extracted fraction: **methanol ≈ acetone (~95%)** > water (73%) > hexane (52%)

ABSORPTION BY SOLVENT EXTRACTS

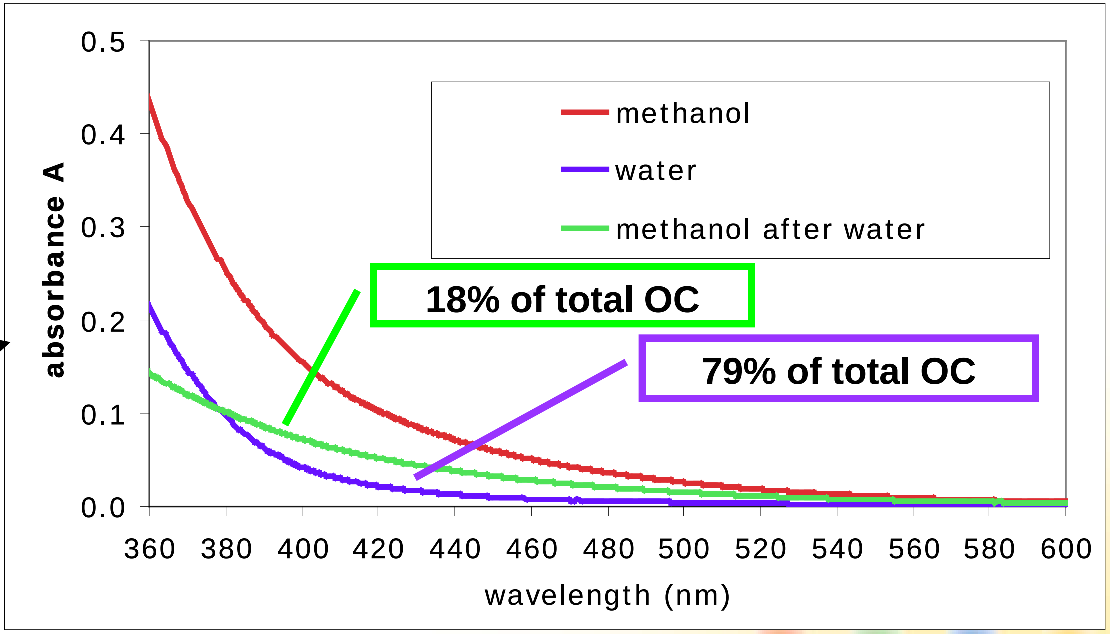


- Average single scattering albedo (green, 530nm): High – 0.95-0.99
- Light absorption by water-soluble organic carbon smaller than that of organic carbon soluble in methanol or acetone.
- What is absorbing most light? – Large molecular weight PAHs with some (but not many) functional groups containing oxygen.

Absorption by water-soluble vs water-insoluble

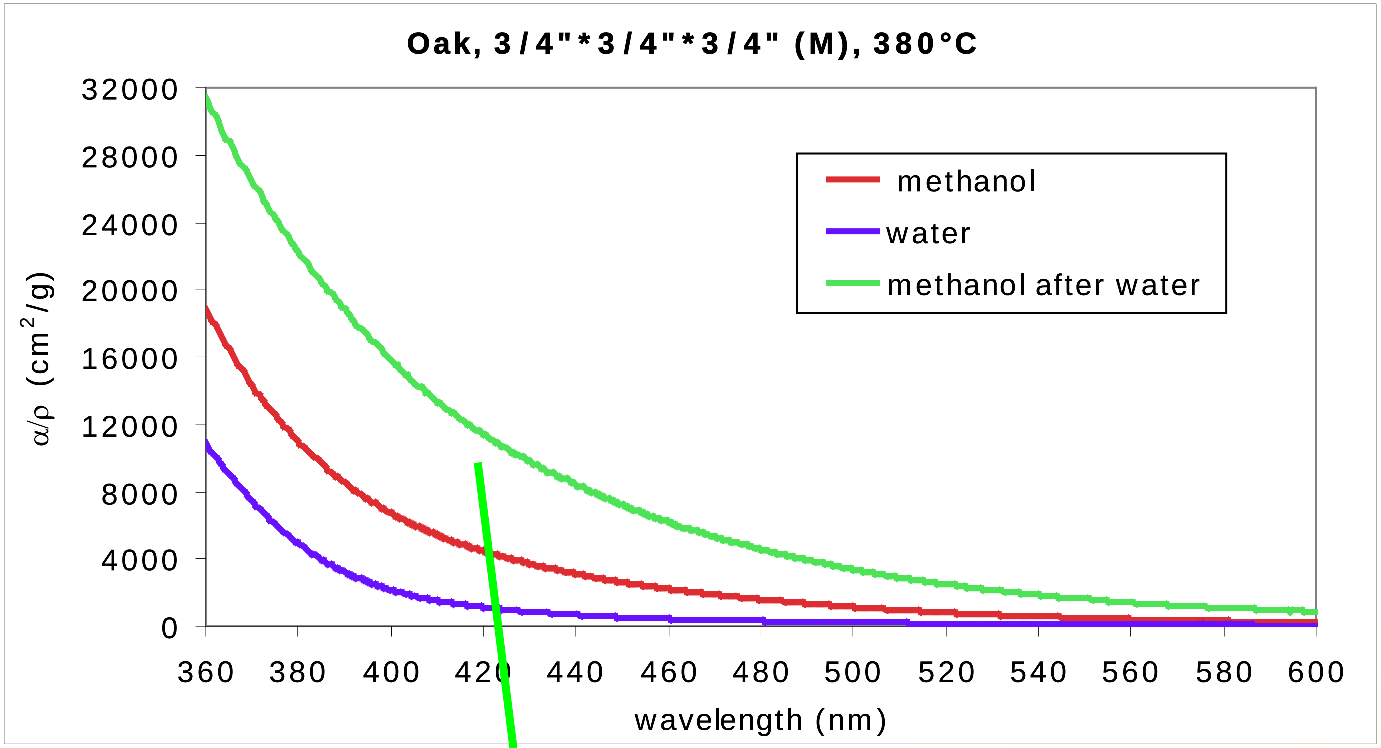
- Different method: Sequential extraction
  - Methanol (most of carbon)
  - Water (water-soluble fraction only)
  - Methanol following water (water-insoluble)

Note: total absorbance



Absorption by water-soluble vs water-insoluble

Note: absorption per C mass

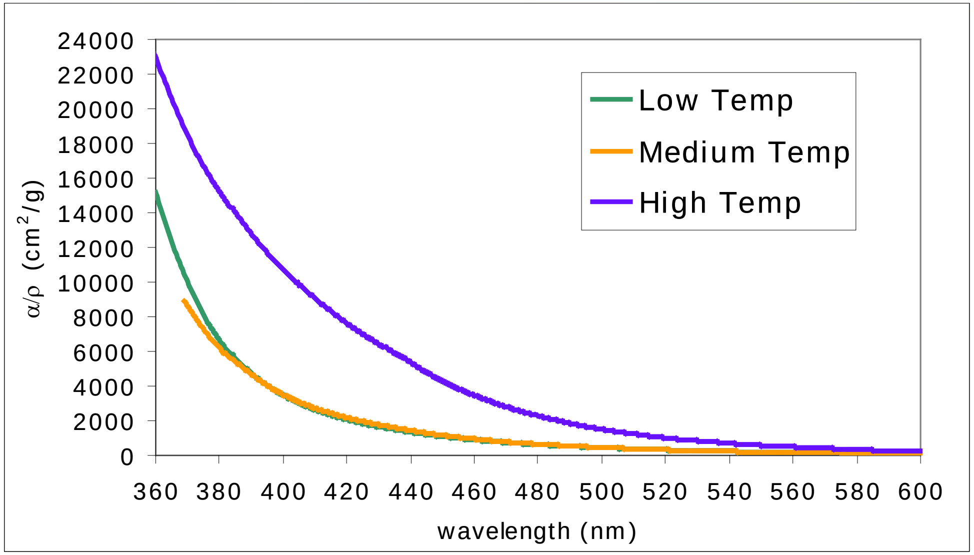


Water-insoluble OC is much more absorbing than water-soluble OC!!!

What affects OC light absorption?

- Temperature at start of combustion?
- Wood size?
- Wood type?

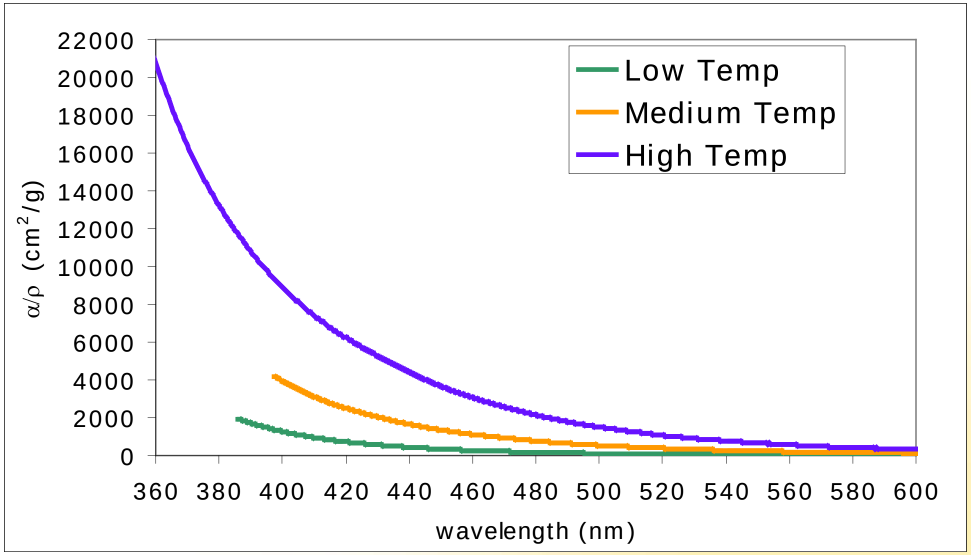
INITIAL TEMPERATURE



Pine, Large size wood

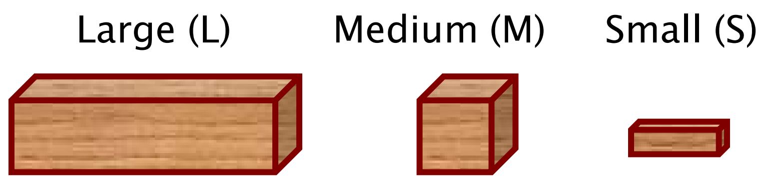
Oak samples have the same trend

Pine, Medium size wood



- Higher temperature = higher absorption per mass (polymerization of volatile matter within wood)
- Especially for smaller size

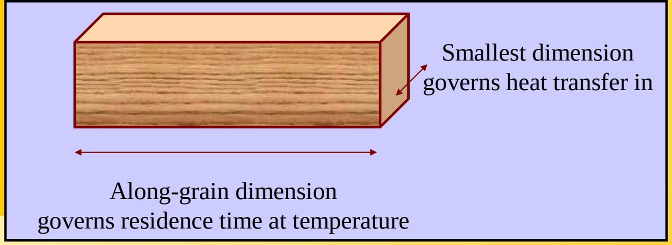
WOOD SIZE

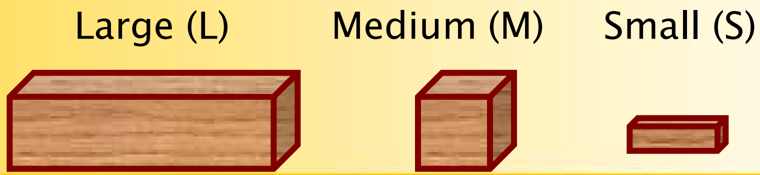


Smallest dimension governs heat transfer in

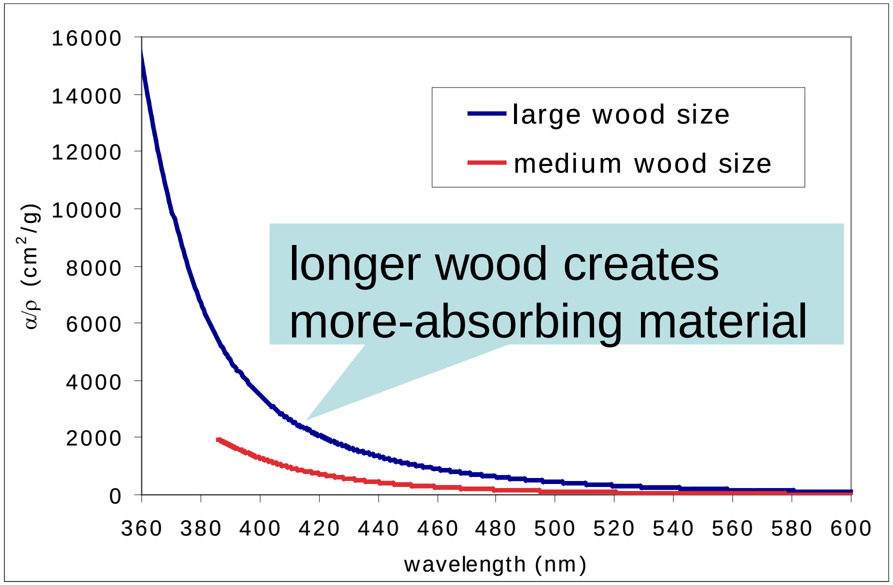
Along-grain dimension
governs residence time at temperature

because escaping volatile matter
travels along grain

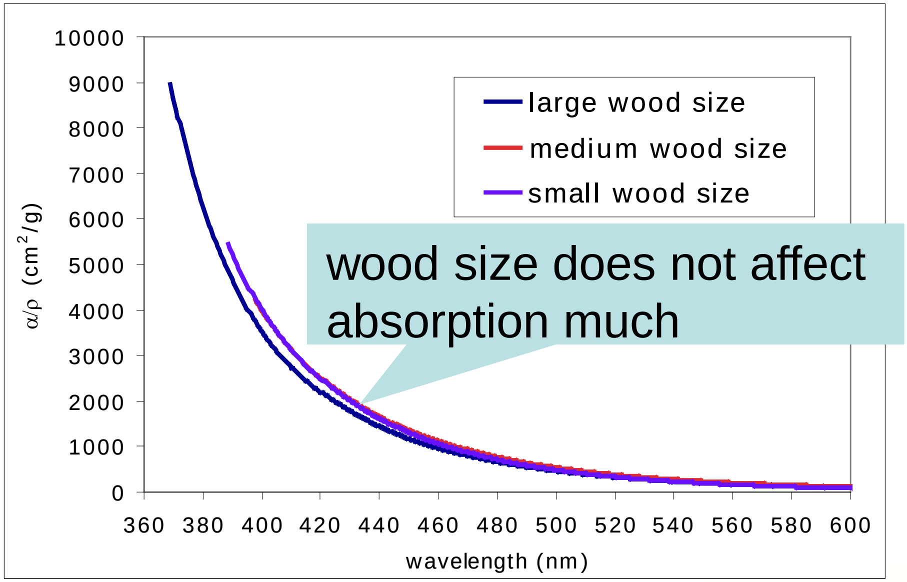




Pine, 200℃



Pine, 380℃



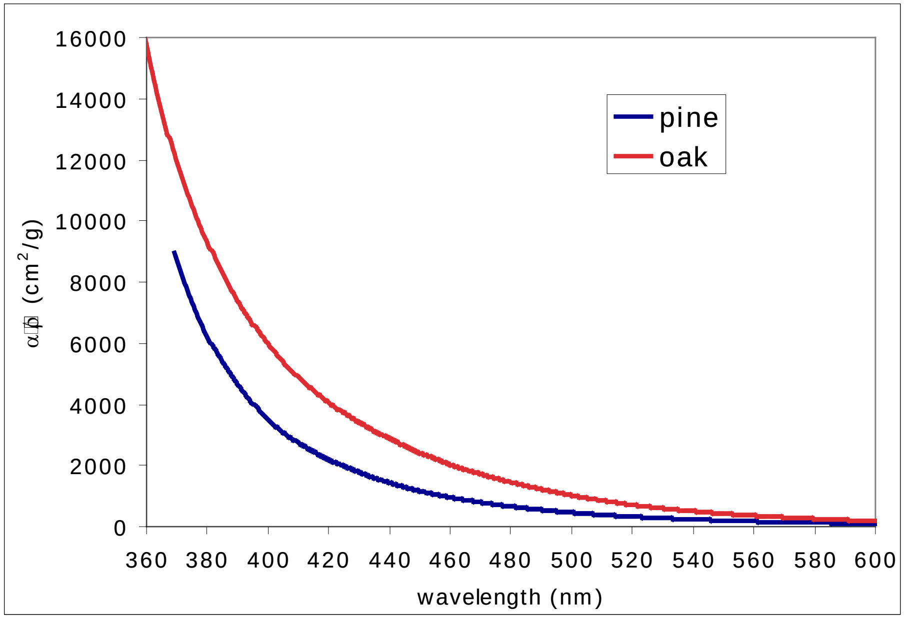
Low T: Longer residence time in the large wood allows polymerization, resulting in greater absorption per mass.

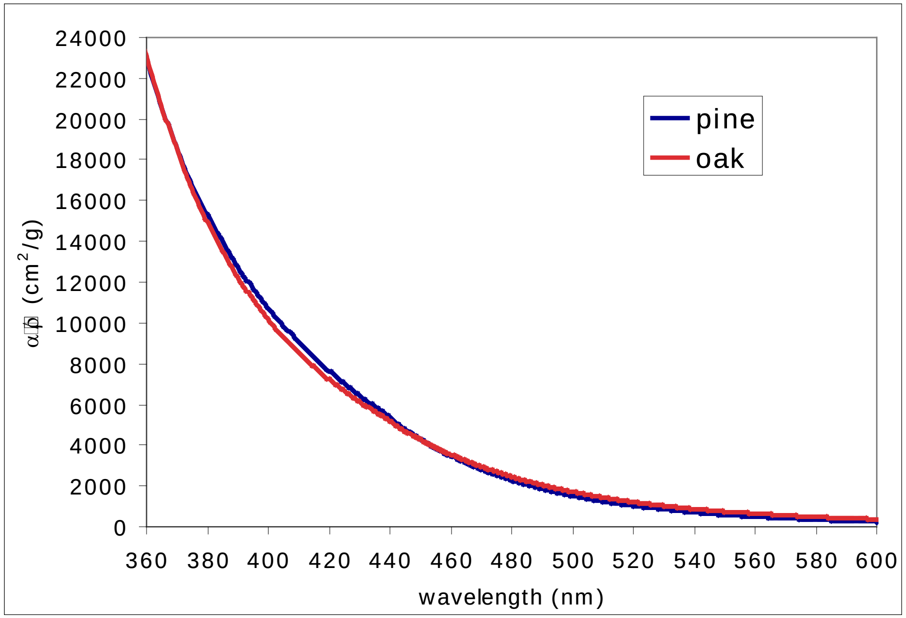
Higher T: Polymerization occurs even without increased residence time.

Oak samples and 500℃ samples have the same trend

WOOD TYPE (Soft wood vs. hard wood)

Large wood size samples





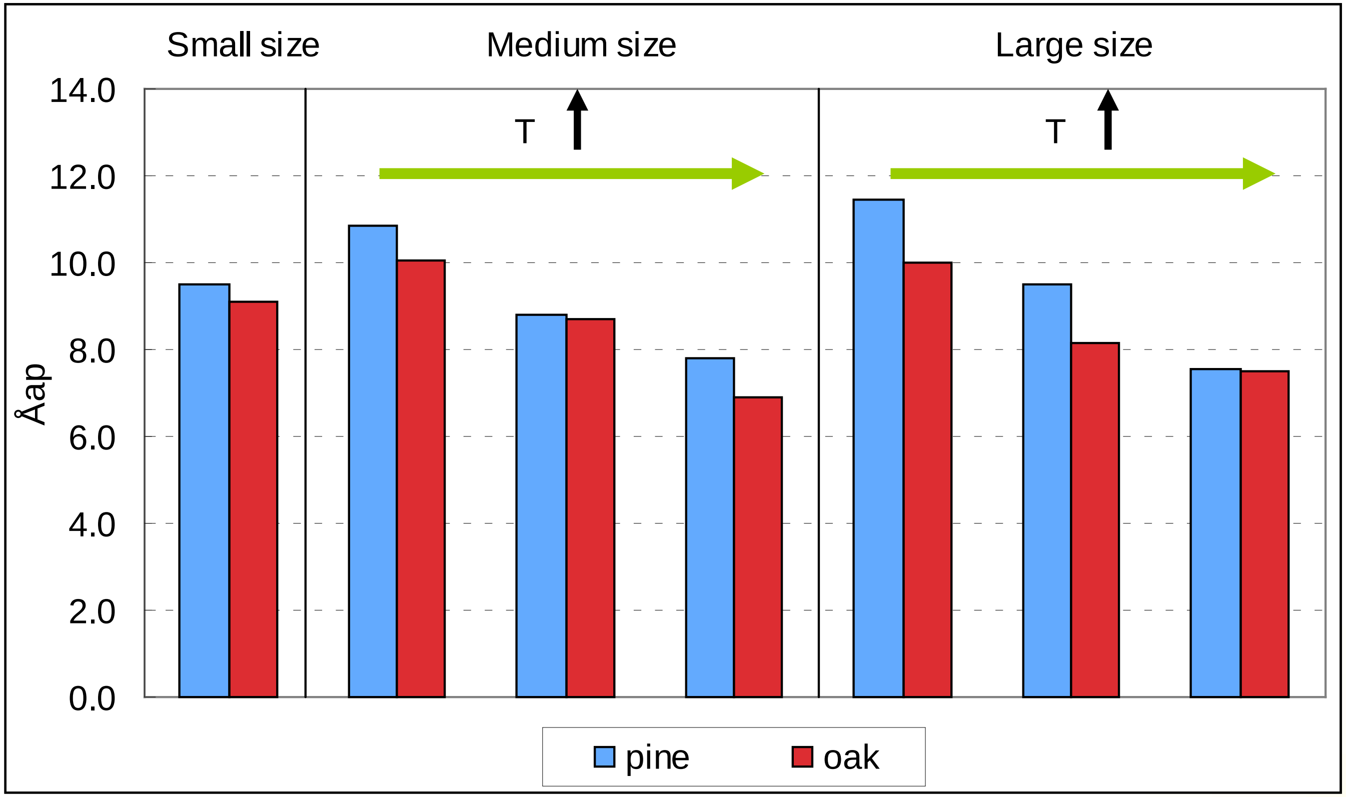
Pine emissions have lower absorption than oak at the medium temperature (380℃)

At the higher temperature (500□) the absorption is identical.

Medium size wood samples have the same trend

Absorption Ångström Exponent (Åap)

$$\alpha(\lambda_1)/\alpha(\lambda_2) = (\lambda_1/\lambda_2)^{-\mathring{A}_{ap}}$$

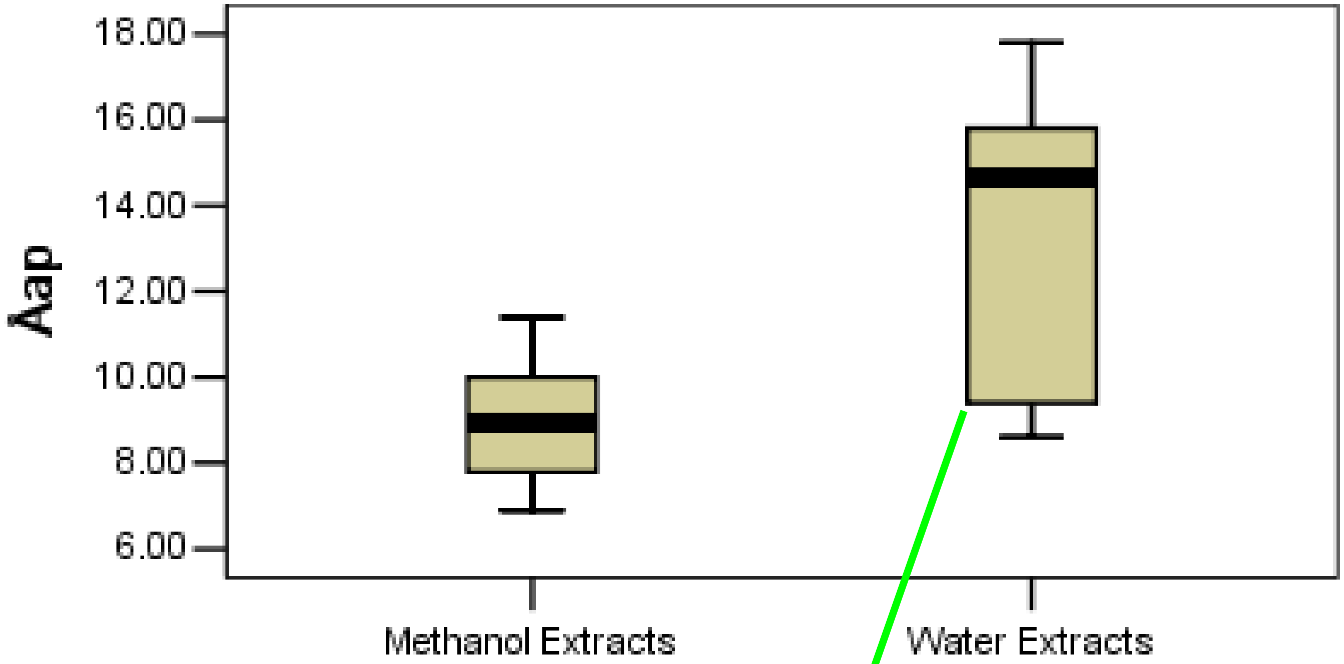


Recall:

Higher T, higher α/ρ

- Linear regression of $\ln(\alpha/\rho)$ against $\ln(\lambda)$, R^2 ranges from 0.989 to 1.000
- Higher Åap values are associated with weakly absorbing particles

Absorption Ångström Exponent (Åap)



Water extracts had much higher Åap

Weaker absorption with stronger wavelength dependence

SUMMARY

- A large fraction of light absorption is attributable to water-insoluble OC, which has some polar functional groups.
- Combustion temperature is the most important factor in determining the light absorption of primary OC.
  - Higher temperatures and longer residence time of volatile matter in wood create higher absorption.
- Higher Åap values are associated with weakly absorbing particles.

Acknowledgements to:

- Bond's Group members
- National Science Foundation

Thank you!

Any Questions?

ABSORPTION PER MASS

Absorption per mass, α/ρ, is the absorption per mass of carbon *in bulk liquid*.

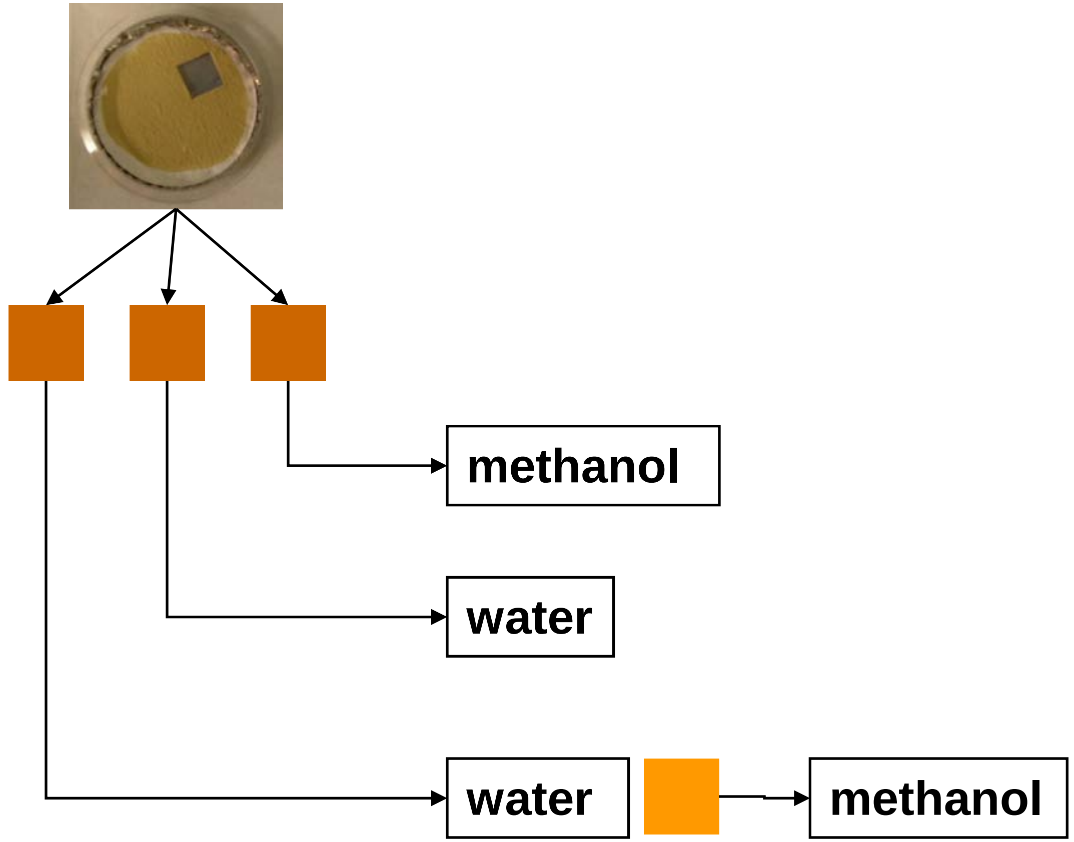
$$\alpha / \rho = \frac{A}{cL} \bullet \ln(10)$$

Where: α = absorption coefficient, cm^{-1}; ρ = density; **A=**absorbance obtained from UV-vis spectrophotometer, dimensionless; **c=**concentration of dissolved organic carbon in extract, g/mL; **L=**light path length, cm

To get absorption for use in models:

- Multiply by ρ
- Calculate imaginary refractive index ($k=\alpha\lambda/4\pi$)
- Use *k* and *same density* in Mie model

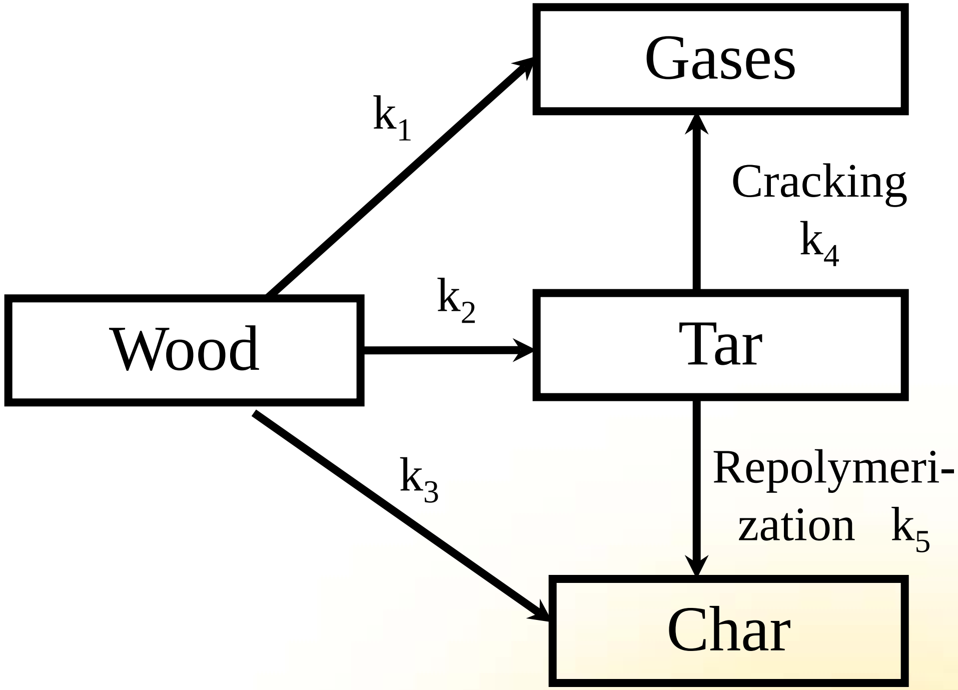
Sequential extraction



Wood Pyrolysis

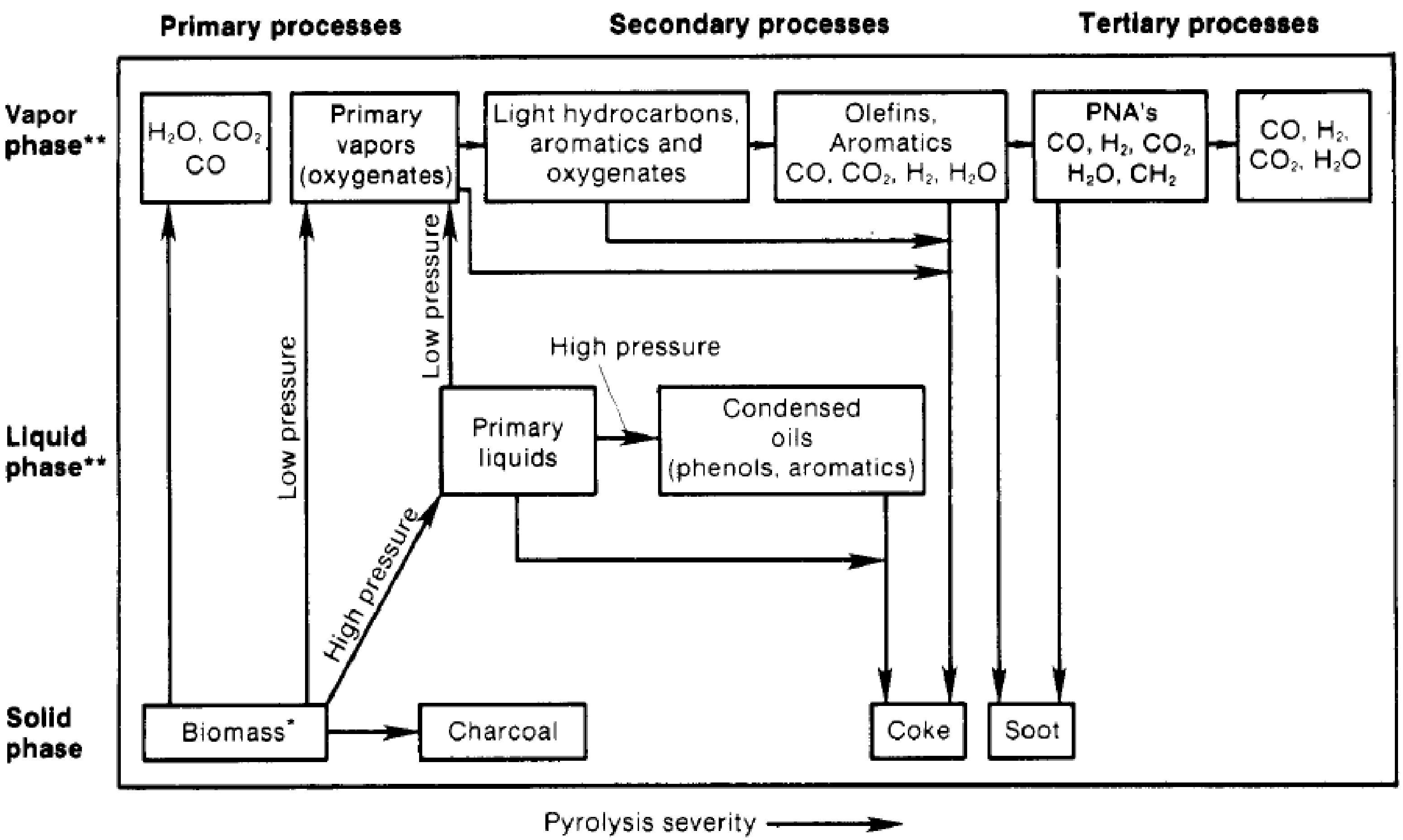
- Complex fuel : cellulose, hemicellulose and lignin = $(C_5H_7O_3)$ + trace elements

- 100-200 ° C
  - Endothermic
  - H2O, simple gases
- 200-280 ° C
  - Weakly Endothermic
  - Char production favored
- 280-450 ° C
  - Exothermic reaction dominate
  - Production of flammable volatiles
  - Cellulose -> tar
- > 450 ° C
  - Only Char remains
  - Converted to CO and CO2



Bryden et al., 2002

Wood combustion process



Evans and Milne, 1986

- Carboxylic acid
- Aromatic groups