



## Black Char and Green Char

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*Publication date:*  
2010

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*Citation (APA):*

Egsgaard, H. (2010). Black Char and Green Char [Sound/Visual production (digital)]. Seminar: Instituto Nacional del Carbon, Oviedo (ES), 17 Feb, 01/01/2010

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# Black Char and Green Char

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Technical University of Denmark, Denmark

$$f(x+\Delta x) = \sum_{i=0}^{\infty} \frac{(\Delta x)^i}{i!} f^{(i)}(x)$$

Other symbols visible:  $\int_a^b$ ,  $\epsilon$ ,  $\theta$ ,  $\sqrt{17}$ ,  $+$ ,  $\Omega$ ,  $\int$ ,  $\delta$ ,  $\epsilon$ ,  $\infty$ ,  $\chi^2$ ,  $\Sigma$ ,  $!$

## **Lay out of talk**

- **Risø National laboratory**
- **Biomass gasification Group**
- **Applications**

## **Lay out of talk**

- **Risø National laboratory**
- **Biomass gasification Group**
- **Applications**

# National Laboratory for Sustainable Energy



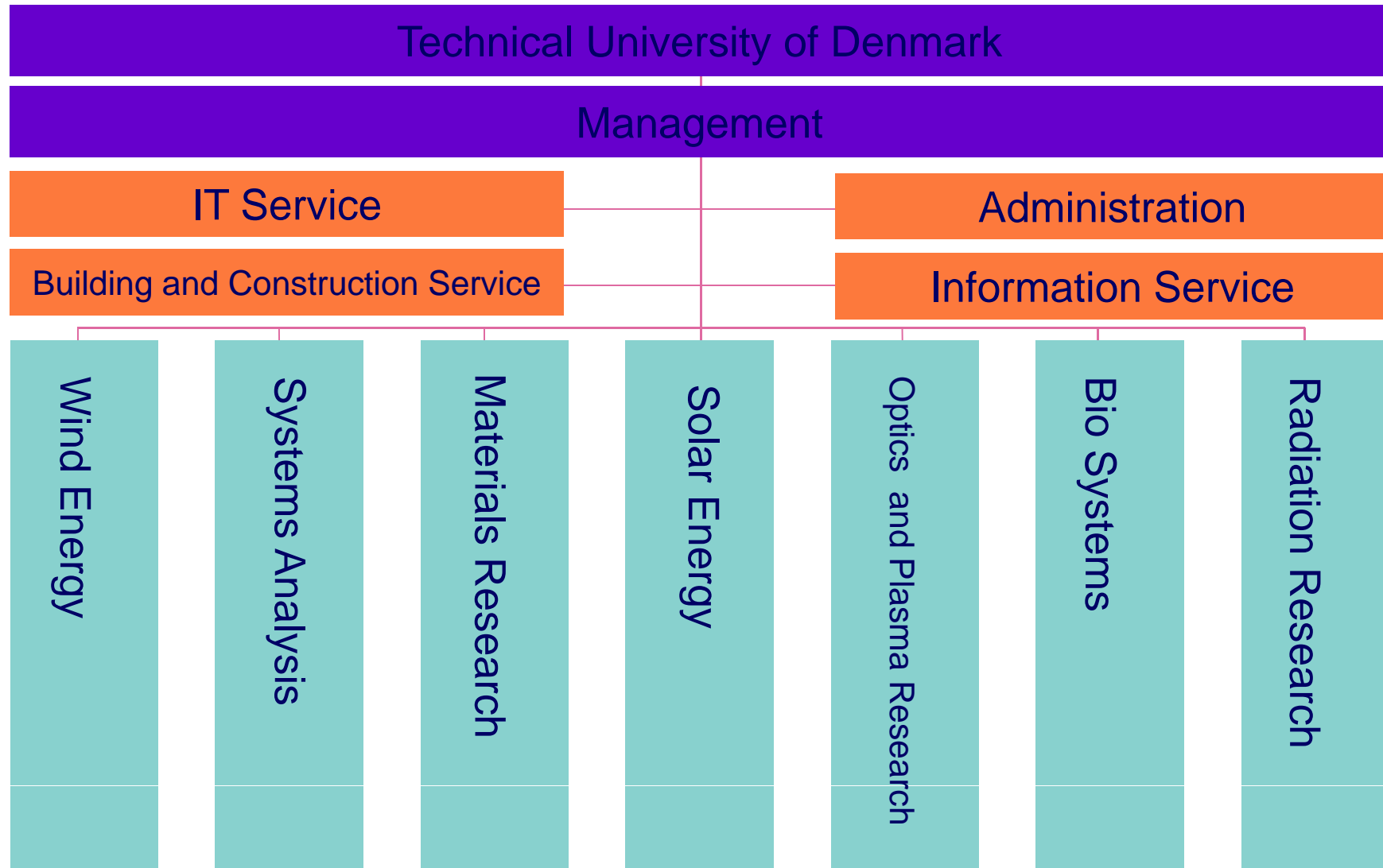
# Risø's history in brief



- **1956** Object: Peaceful utilization of nuclear energy
- **1976** Object: Nuclear energy and other energy sources
- **1986** Object: Energy
- **1990** Object: Technological research and development with energy as main focus area
- **1994** State-owned enterprise
- **2000** The last nuclear reactor is decommissioned
- **2007 merged with the Technical University of Denmark**



# Organisation



# Biomass Gasification Group

## Research Areas

- **Gasification processes**Two-stage fixed bed gasification (Viking)
- **Low temperature fluid bed gasification (LT-CFB)**
- **Pyrolysis processes**
- **Gas cleaning**
- **Particle filtration**
- **Tar reduction through partial oxidation and tar char reactions**



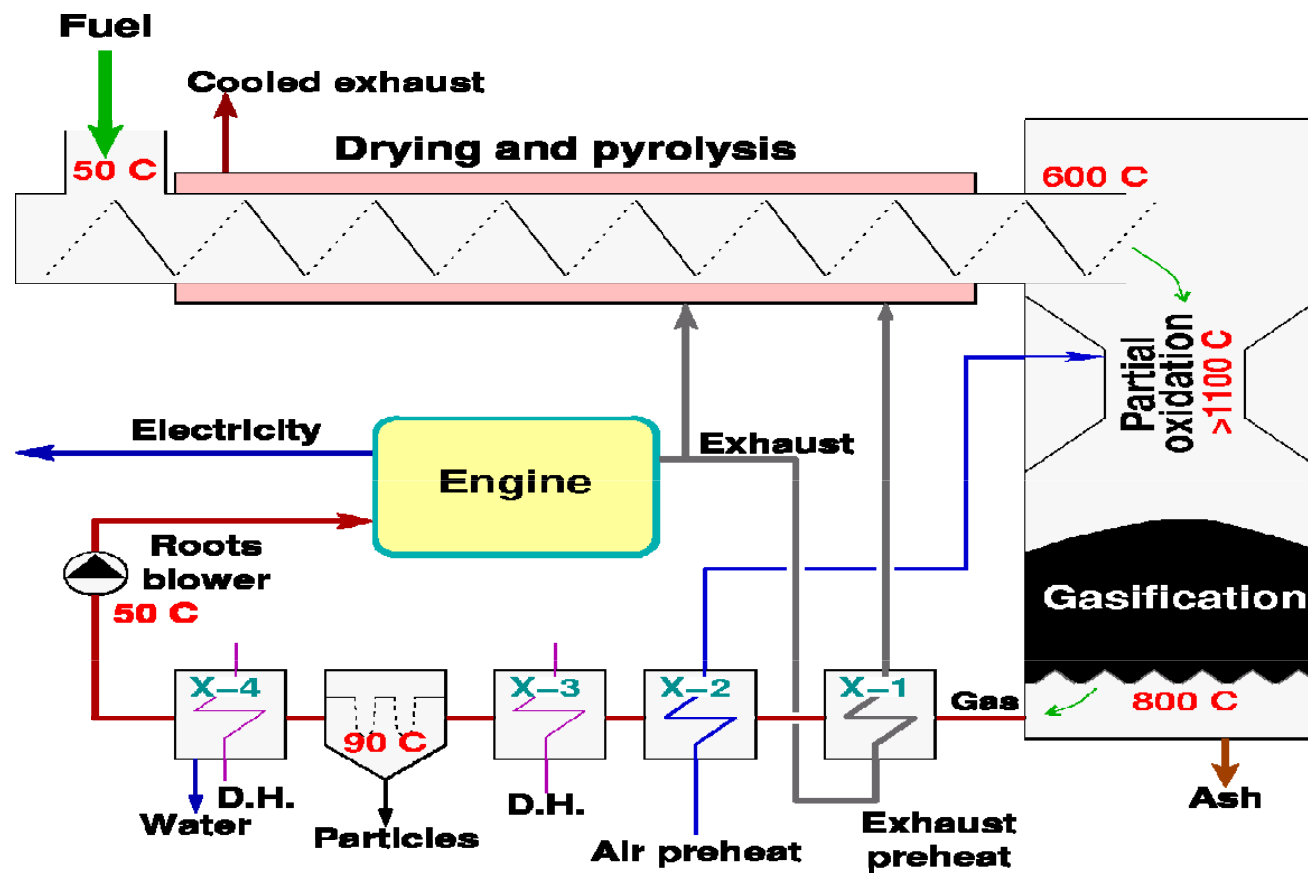
# Thermal Gasification at Risø DTU

## The Viking TwoStage Gasifier



# Thermal Gasification at Risø DTU

## The Viking TwoStage Gasifier



# **New Research Areas**

## **Torrefaction of Biomass and Waste**

**Torrefaction is a new thermo-chemical pretreatment primarily used for upgrading the fuel properties of biomass.**

**The process is characterized by an operating temperature of 200 – 300 °C, absence of oxygen and low heating rates.**

# New Research Areas

## Fundamental Understanding of Pelletization

### Objectives:

- **Flexible and effective utilization of biomass as fuel**
- **Standardised fuel with clean burning properties**
- **Upgrading of waste residues to high value fuel**
- **New knowledge in the border area between energy engineering and wood science**

# On the chemistry of char

## *An isotope study*

# **The potential of isotopes in chemistry**

**Isotopic labelled compounds are close to the ideal chemical internal standard**

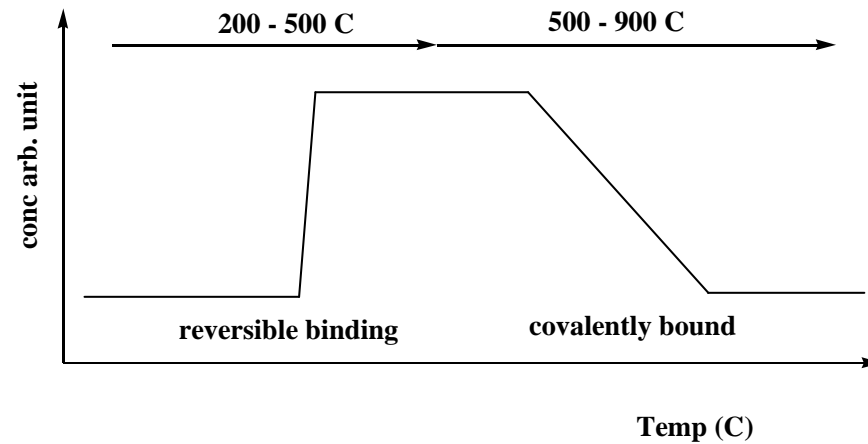
**Isotopes may be used to disclose hidden reactions**

- **Tracer studies**
- **Fine variations in the natural abundance of isotopes**





# Reactivity of char

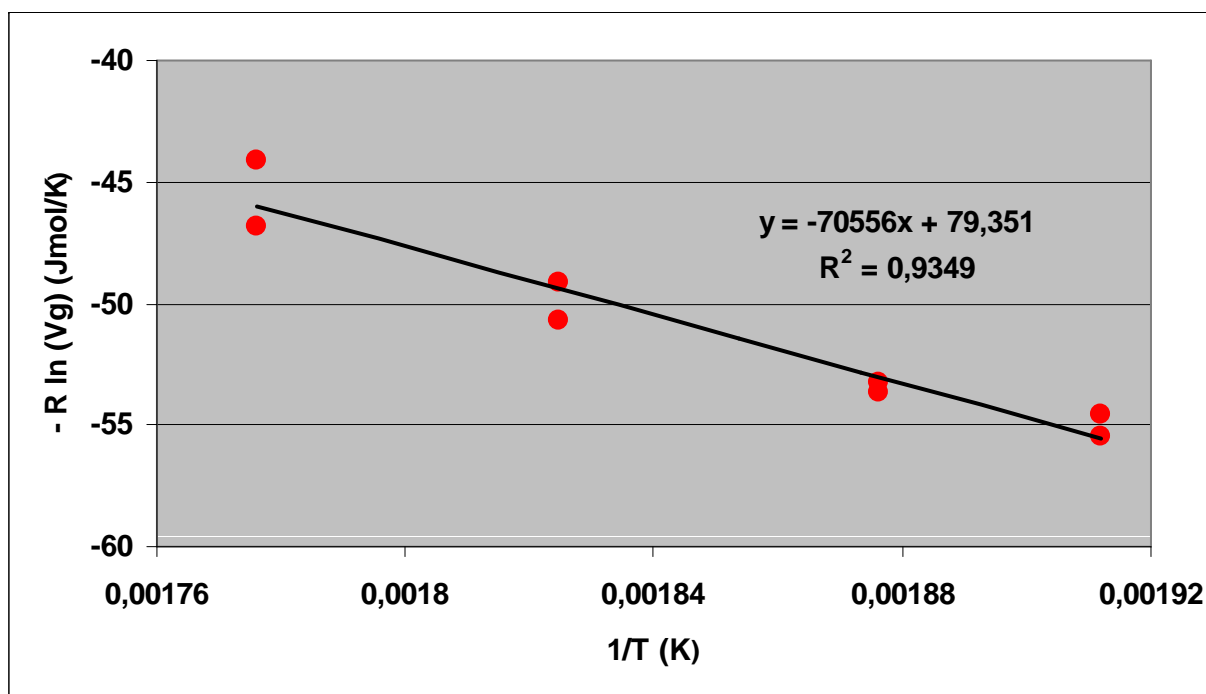


## Experimental techniques :

**Reversible binding by high temperature GC (200-400 °C)**

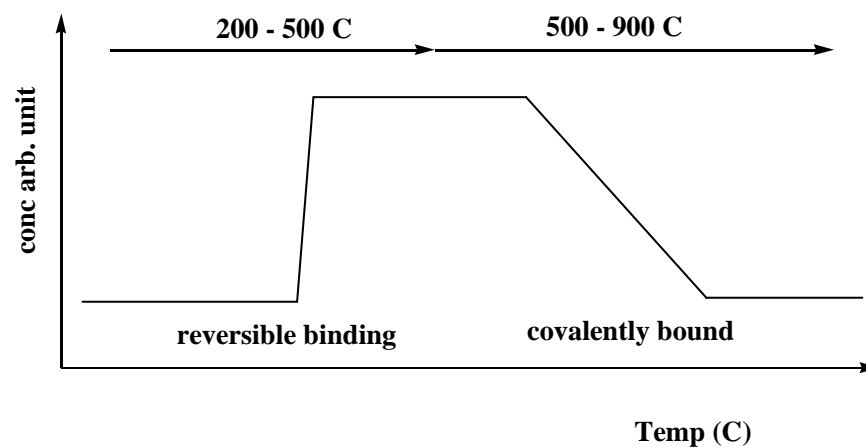
**Covalent binding by dedicated oven systems**

## Low temperature binding of benzene to char



**Adsorption enthalpy: -71 kJ/mol**

# Reactivity of char

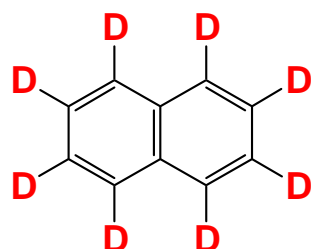
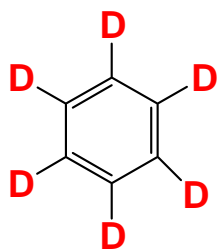


## Experimental techniques :

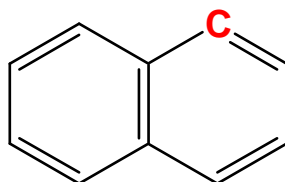
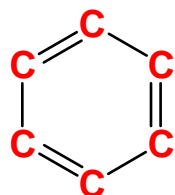
**Reversible binding by high temperature GC (200-400 °C)**

**Covalent binding by dedicated oven systems**

## Stable isotope experiments

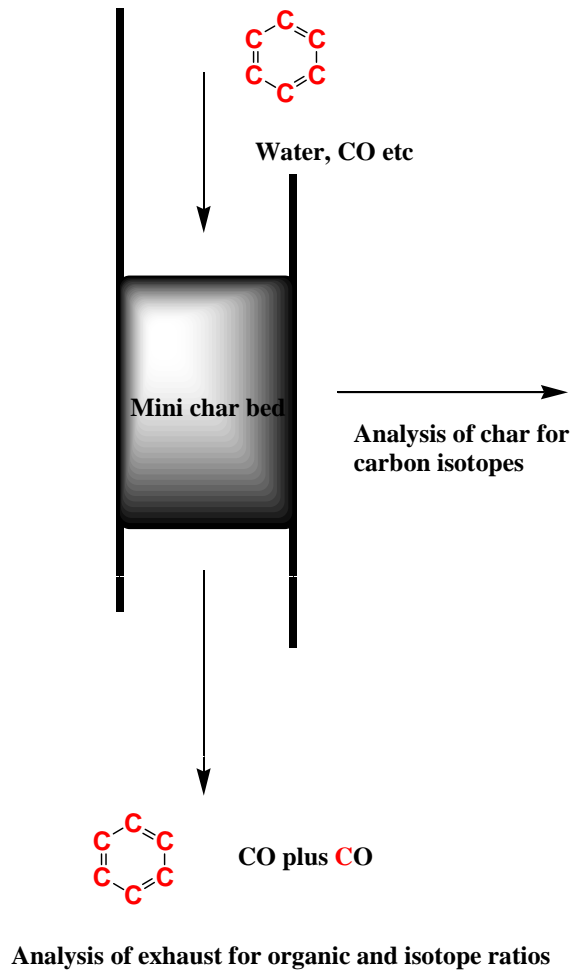


**Deuterium labeling to study the presence of labile hydrogen's in char.**

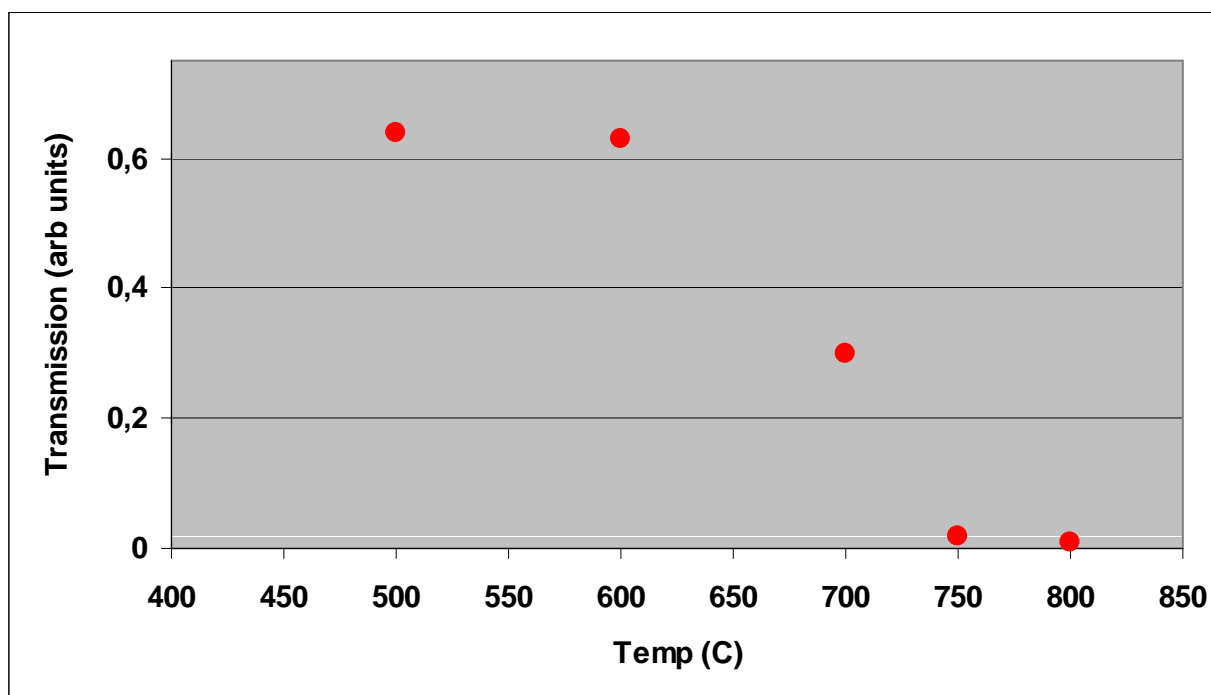


**Carbon labeling to study the built up of carbon in char**

# Isotope studies with char

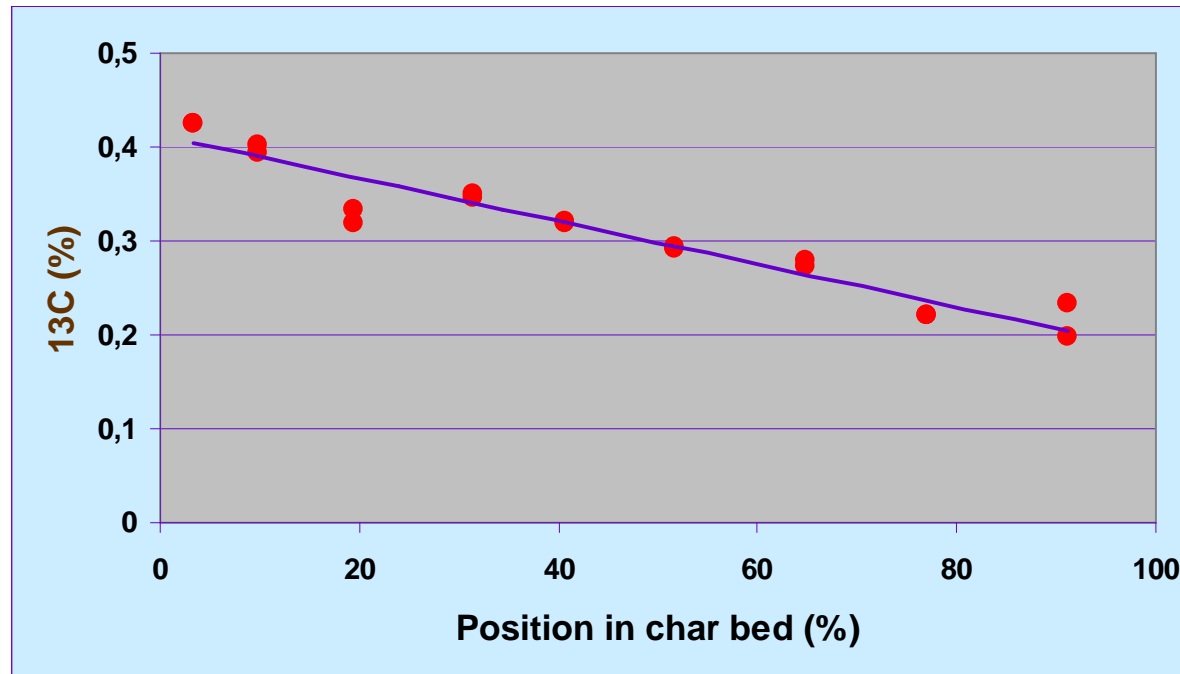


## High temperature studies of char



**Transmission of benzene as function of temperature**

## Carbon isotopes in char



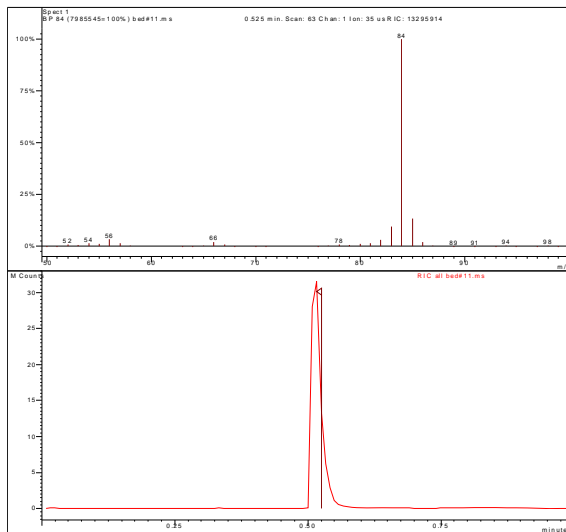
Temperature 700 °C; transmission 35 %; char bound 50 %



# High temperature studies of char

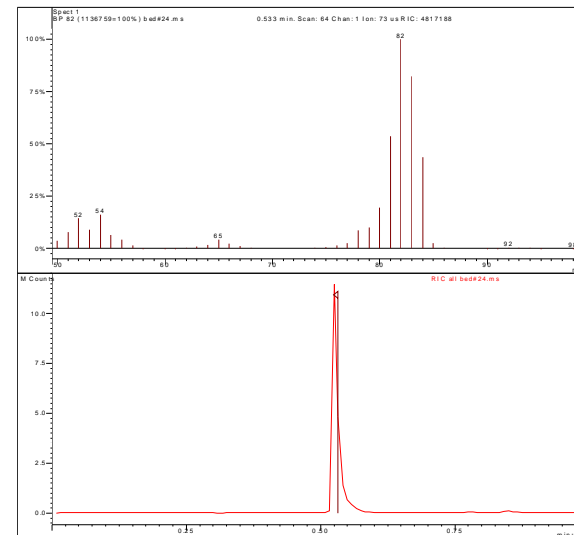
## Chromatogram Plot

File: c:\satum\data\gcbed\bed#11.ms  
 Sample: RUN #2 --INTET KOKSLEJE -- 800C 10  
 Scan Range: 1 - 239 Time Range: 0.01 - 1.99 min  
 Sample Notes: RUN #2 INTET KOKSLEJE 800C 62 MIN  
 Operator: HEEG  
 Date: 27-07-05 14:34



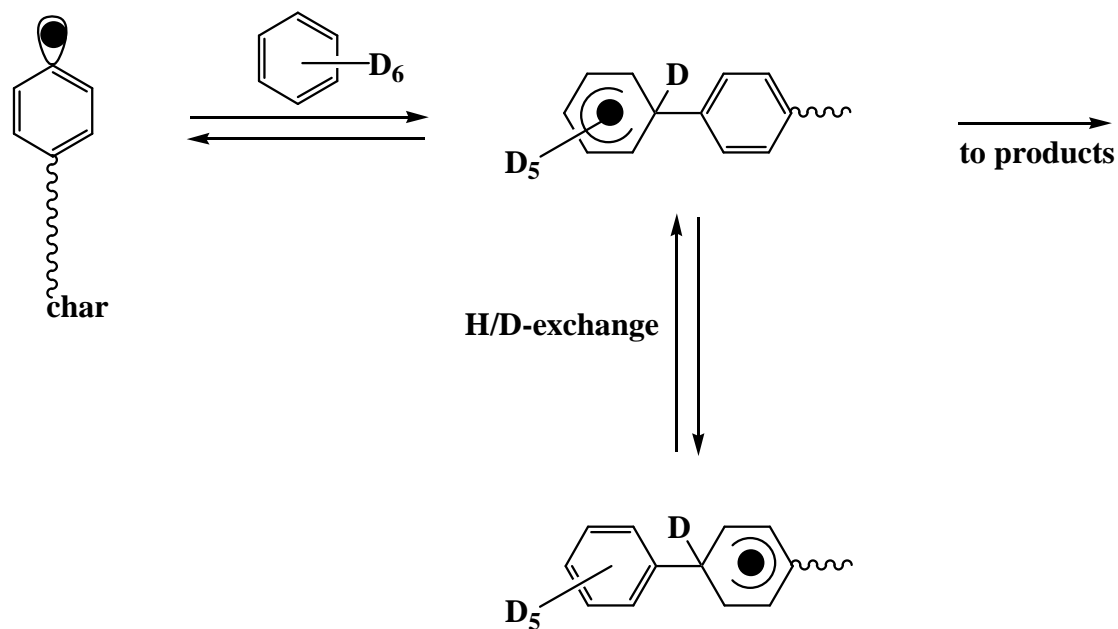
## Chromatogram Plot

File: c:\satum\data\gcbed\bed#24.ms  
 Sample: RUN #5 600 C ISOTOPES OM LY  
 Scan Range: 1 - 240 Time Range: 0.01 - 2.00 min  
 Sample Notes: RUN # 600 c ISOTOPES ONLY  
 Operator: HEEG  
 Date: 31-07-05 16:02



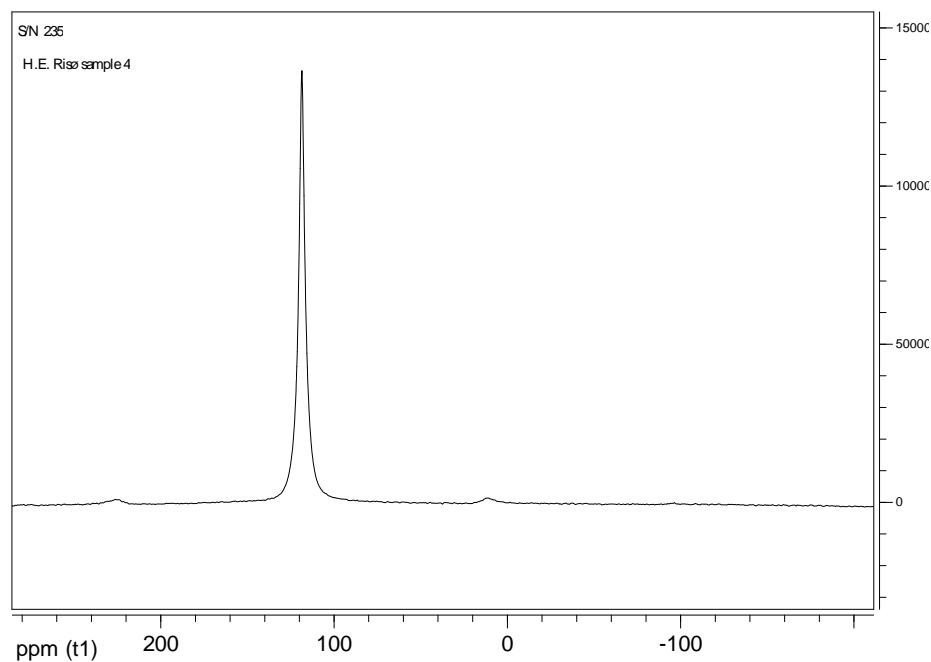
**GC/MS analysis of D<sub>6</sub>-benzene without char at 800 °C (left panel) and with char bed at 600 °C (right panel).**

# High temperature studies of char



**Free radical mechanisms are most likely to account for the isotope exchange and binding.**

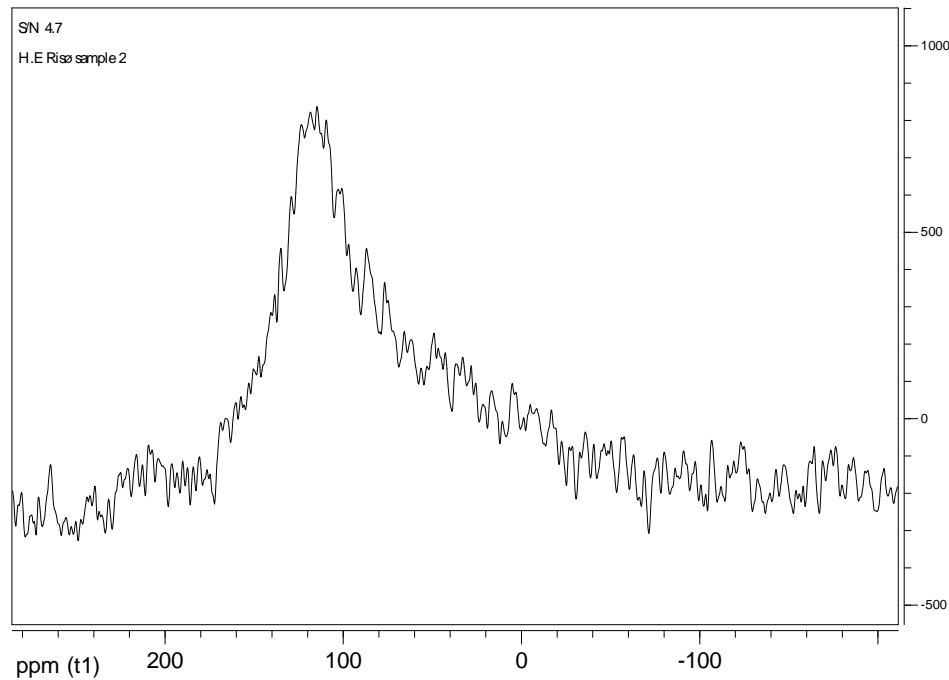
# High temperature studies of char



**$^{13}\text{C}$ -solid-state NMR spectrum of char loaded with  $^{13}\text{C}_6$ -benzene at 200 °C**

**Solid-state NMR has been used to visualise the nature of char-bound benzene.**

# High temperature studies of char



**<sup>13</sup>C-solid-state NMR spectrum of char  
loaded with <sup>13</sup>C<sub>6</sub>-benzene at 800 °C**

**Solid-state NMR has been used to visualise the nature of  
char-bound benzene.**

## High temperature studies of char

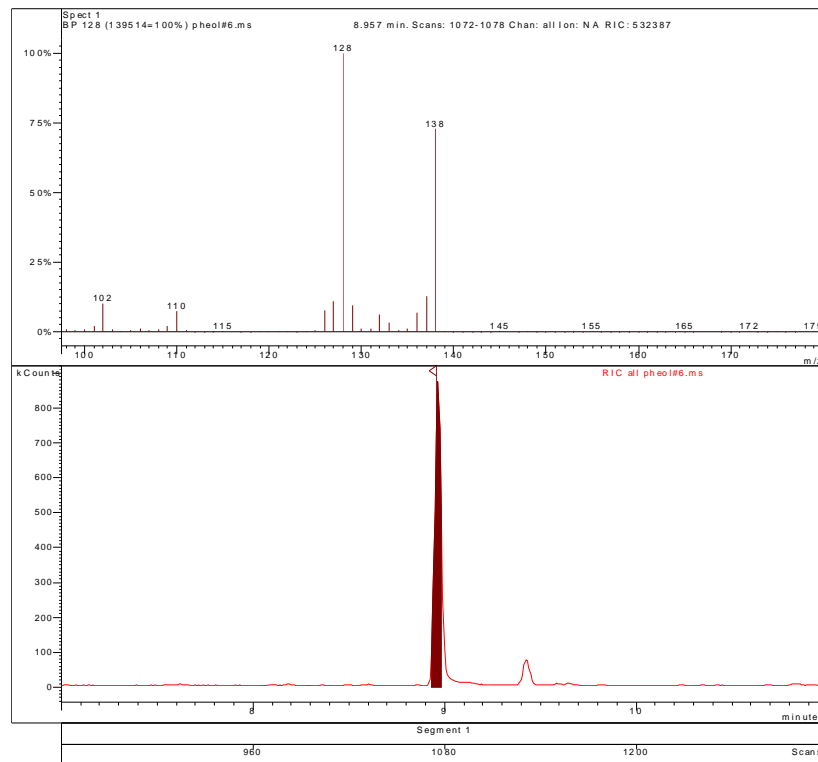
**Maintaining this covalently bound benzene/char system for additional 16 hours leads to a reduction of the solid-state NMR signal.**

**This is tentatively assigned the subsequent transformation of the covalently bound benzene into the rigid part of the char exhibiting longer relaxation times for the carbon nucleus and, hence, lower signal strength**

# High temperature chemistry of phenol

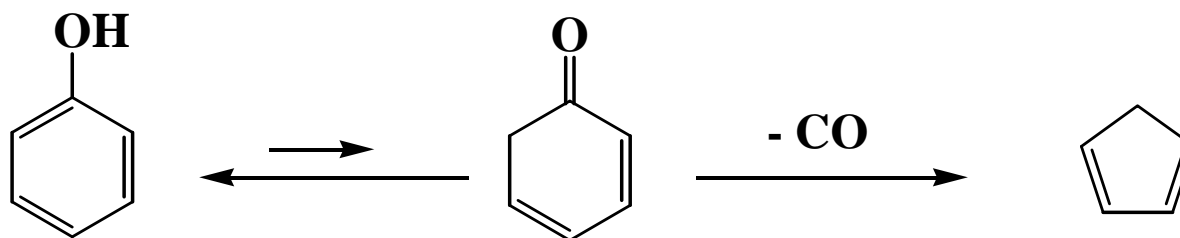
## Chromatogram Plot

File: c:\saturn\data\gcois\pheel#6.ms  
Sample: 13C PHENOL OPSAMLING RUN 5 DOUBLE Operator: HAWO  
Scan Range: 1 - 3600 Time Range: 0.00 - 30.00 min. Date: 07-01-08 11:27  
Sample Notes: 13 C PHENOL OPSAMLING RUN 5 DOUBLE SPIKED (HELE PROEVEN)



**GC/MS analysis of naphthalene generated during loading of  $^{13}\text{C}_6$ -phenol at 800 °C. The sample is spiked with naphthalene (m/z 128)**

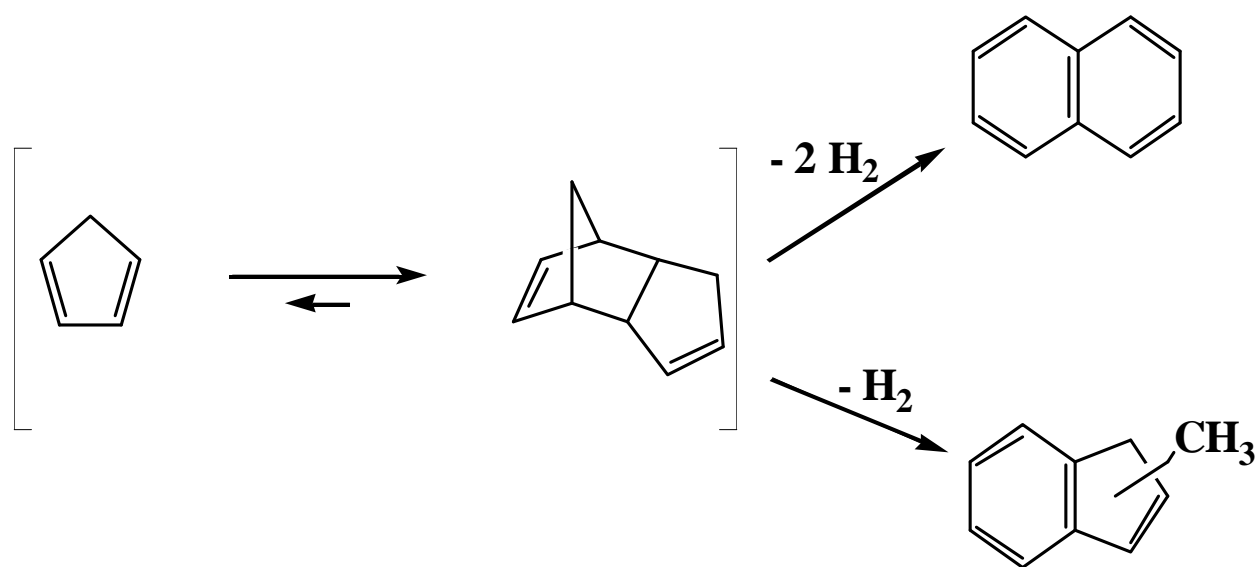
## High temperature chemistry of phenol



The rate determining step in the pyrolysis of phenol

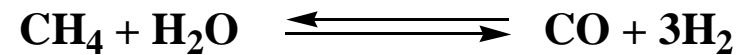
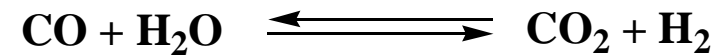
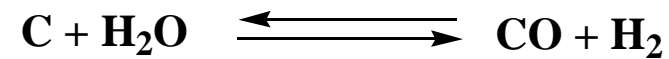


# High temperature chemistry of phenol



Formation of naphthalene and methylindenes

## Gasification - The use of $^{13}\text{C}$ -labelled char

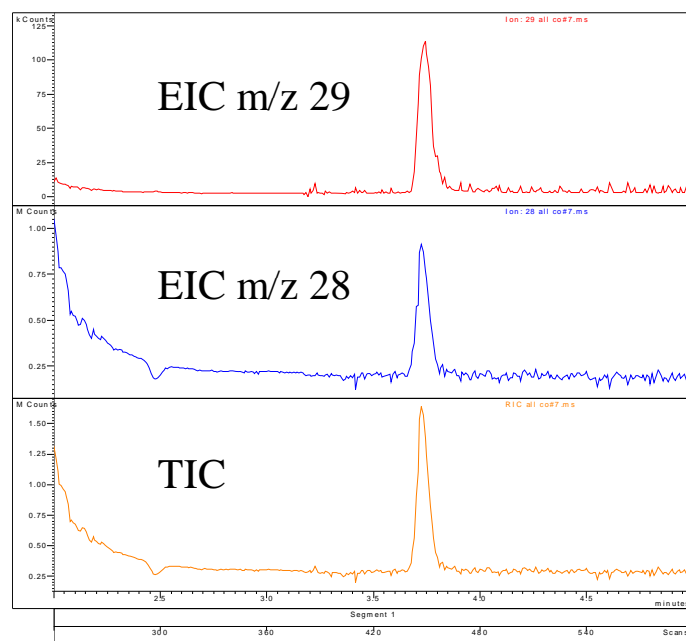


The gaseous products are formed as a result of a series of coupled reactions

# Gasification - The use of $^{13}\text{C}$ -labelled char

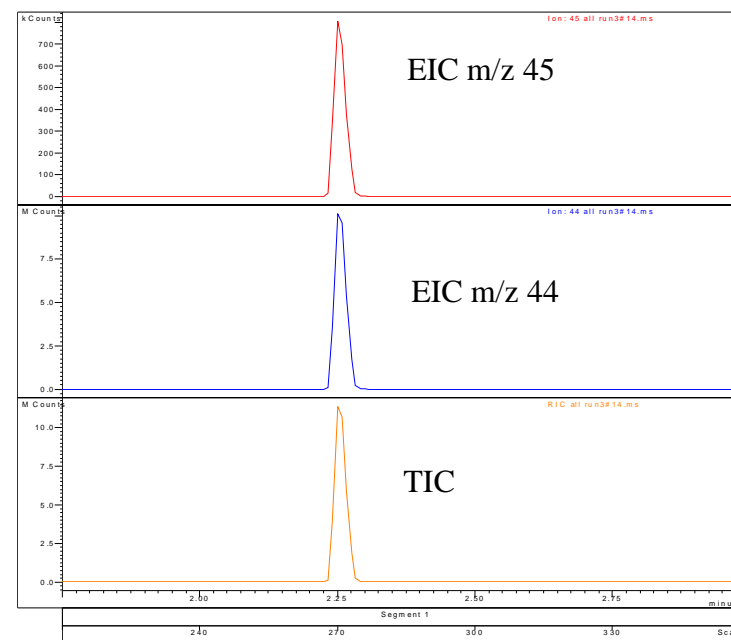
## Chromatogram Plots

File: c:\satur\data\gfciso\co#7.ms  
 Sample: CARBON MONOXID ANALYSE RUN 3 PIPE  
 Scan Range: 1 - 1199 Time Range: 0.01 - 9.99 min.  
 Sample Notes: CARBON MONOXID ANALYSE RUN 3 PIPETTE 2  
 Operator: HAWO  
 Date: 20-02-07 14:42



## Chromatogram Plots

File: c:\satur\data\gfciso\run3#14.ms  
 Sample: RUN #3 PIPETTE 2 CO2  
 Scan Range: 1 - 599 Time Range: 0.01 - 4.99 min.  
 Sample Notes: RUN #3 PIPETTE 2 CO2  
 Operator: HAWO  
 Date: 16-02-07 15:14



**Determination of  $^{13}\text{C}$  abundance of carbon monoxide and carbon dioxide.**

## Conclusion – isotope study

**A trend in the binding efficiency, namely:  
benzene < naphthalene < phenanthrene was found.**

**Phenol behaved different from the other aromatic compounds studied. It partly undergoes decarbonylation leading to formation of naphthalene in a specific and well defined reaction pathway.**

**Isotope exchange reactions provided some evidence for a free radical mechanism as being responsible for the binding the compounds to the char bed.**

**Gasification of the labelled chars suggests that 95 % the incorporated carbon (benzene) loss its chemical history in the char bed.**

## From Biomass to Bio-char

Application of bio-char to soil has been proposed as a significant and long-term sink for carbon dioxide in terrestrial ecosystems.

An improved understanding of the mechanisms involved in bio-char application to soil is crucial in the ongoing debate about the addition of bio-char to soil to offset human-induced climate change.



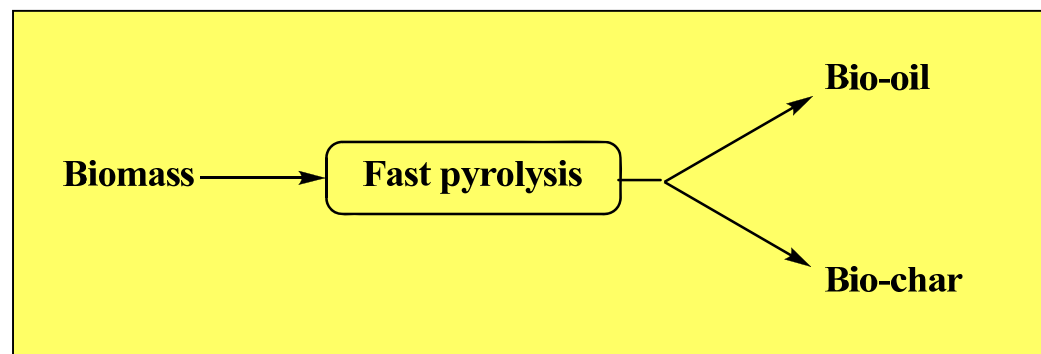
**Black is the new green**

## From Biomass to Bio-char

Bio-char is the carbon-rich product obtained by heating biomass at oxygen starvation and relatively low temperature ( $< 700\text{ }^{\circ}\text{C}$ ).

We are currently studying the co-production of bio-oil/bio-char based on wheat straw using an innovative fast pyrolysis centrifuge in the temperature range  $475 - 575\text{ }^{\circ}\text{C}$  and a residence time in the order 1 s.

N. Bech, N. K. Dam-Johansen, P.A. Jensen,.  
Pyrolysis Method and Apparatus,  
PCT Application WO 2006/117005, 2006.



## Summary

**We have developed methods for characterization of bio-char/bio-oil based on analytical flash pyrolysis in combination with GCMS.**

**These methods allow:**

- ❑ Simulation of bio-oil composition**
- ❑ Determination the origin of specific compound classes found in the bio-oil**
- ❑ Determination of residual organic compound classes in bio-char**

# Instrumentation – Analytical flash pyrolysis

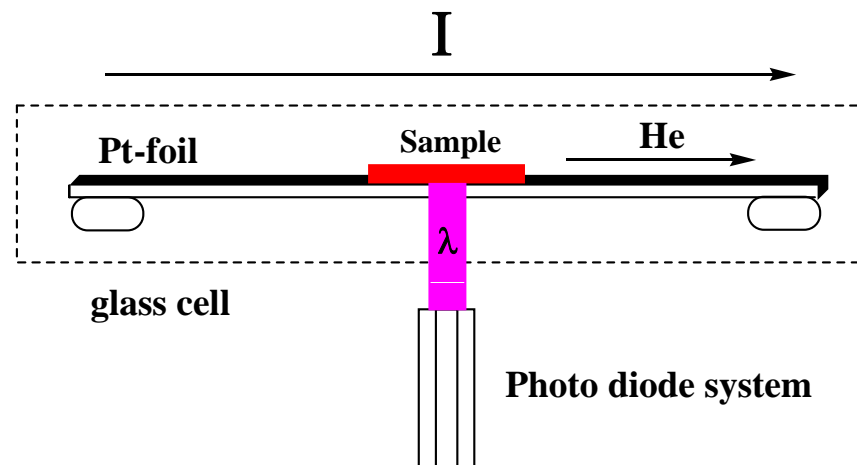
## Analytical flash pyrolysis

Controlled fast heating is achieved by two DC pulses:

- I. 30- 40 A for 5-10 ms
- II. 5-10 A for 1-2 s



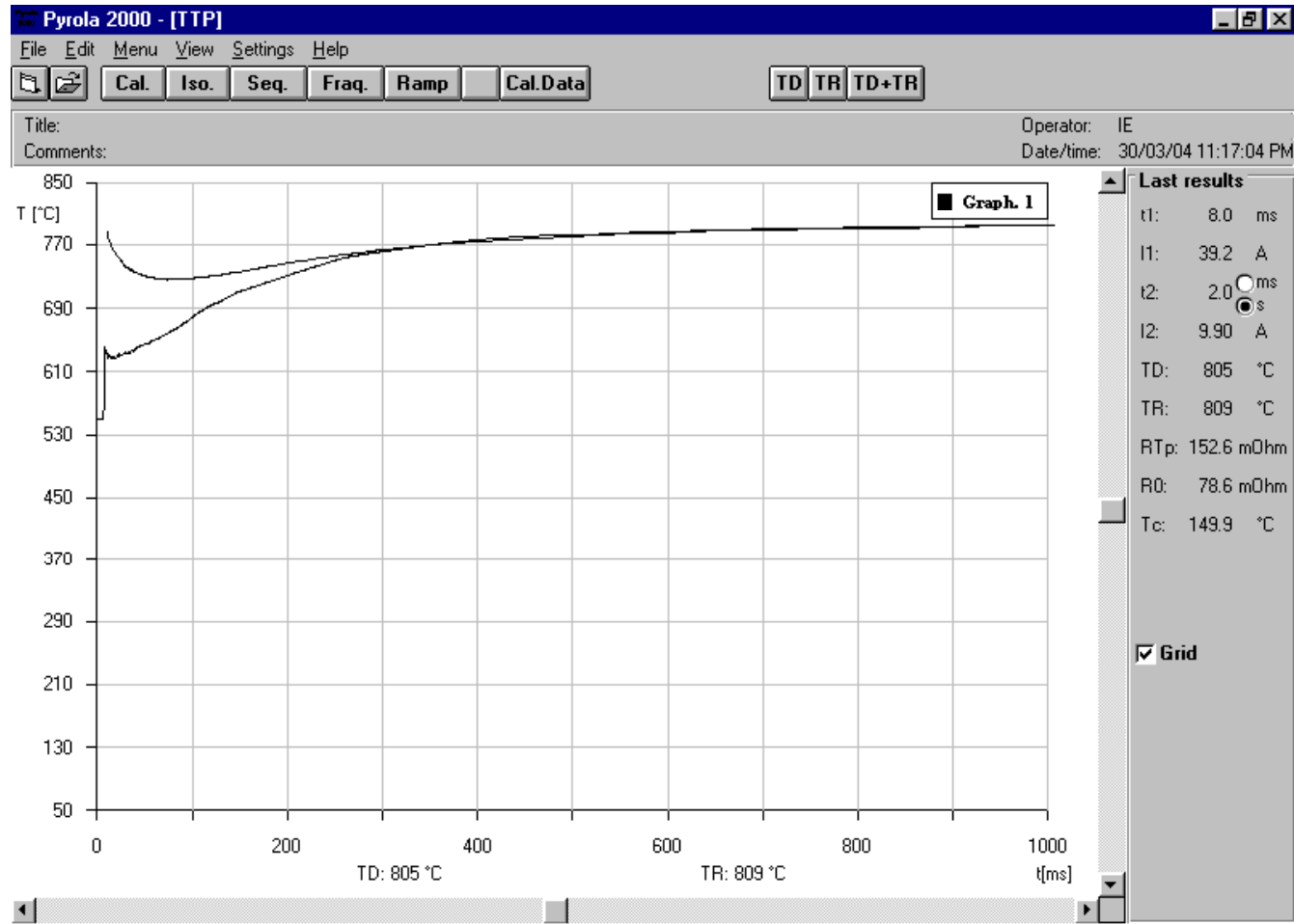
**Ohmic heating** using platinum foil  
(14 x 3 x 0.03 mm)





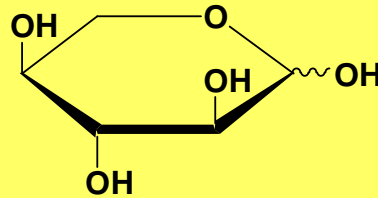
# Instrumentation – Analytical flash pyrolysis

## Process-near characterization

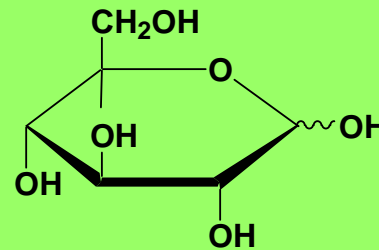


# Biomass – dominant substructures

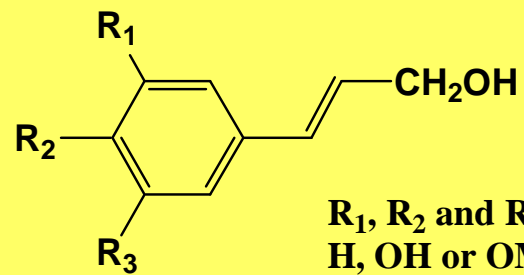
**Hemi-cellulose**



**Cellulose**

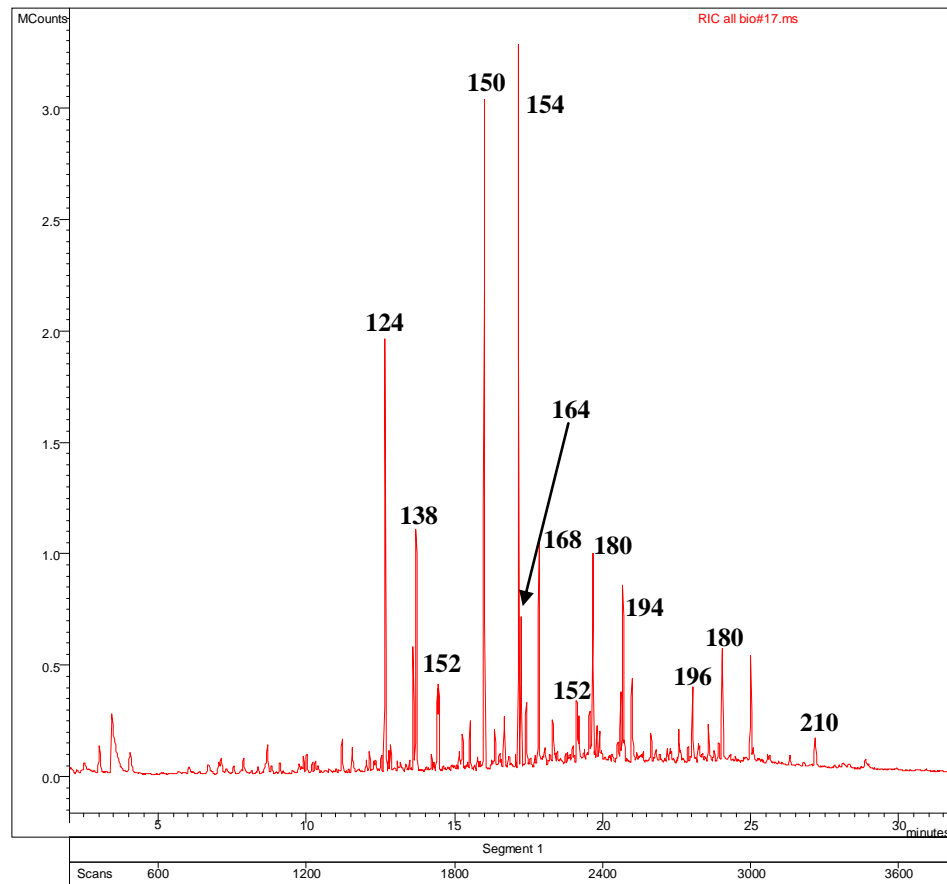


**Lignin**



**R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> :  
H, OH or OMe**

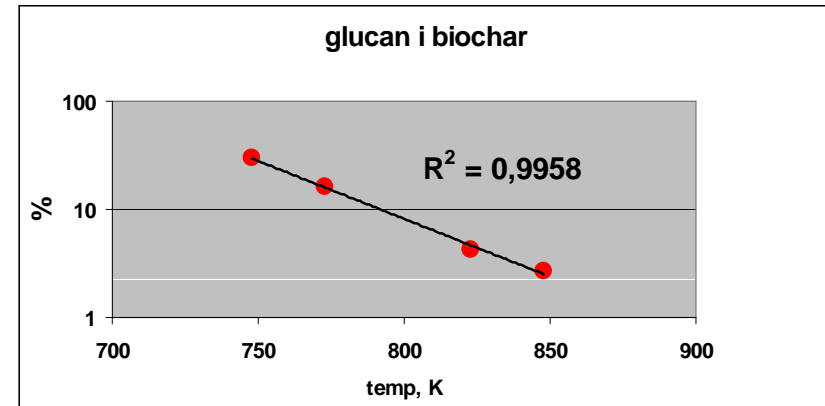
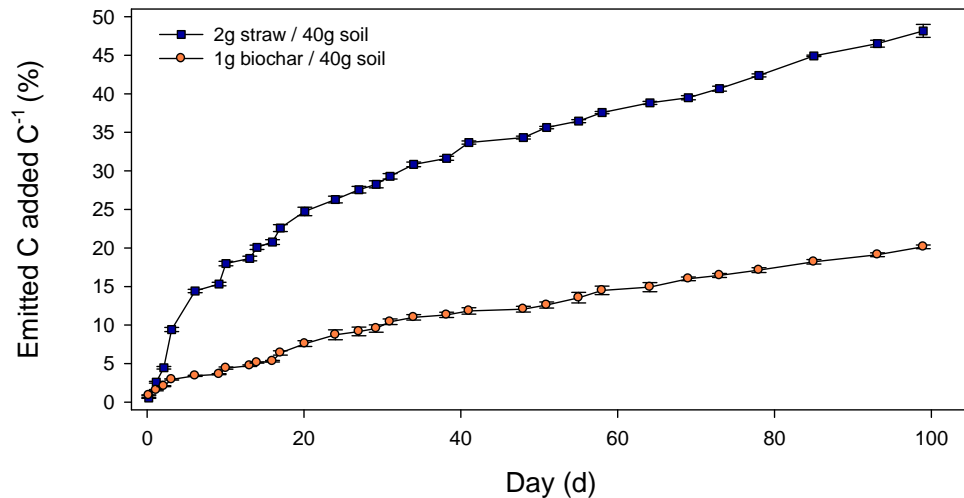
# Analytical flash pyrolysis – Lignin



Analytical flash pyrolysis  
at 600 °C and 2 s of lignin

Backbone	H	Me	Et	HC=CH <sub>2</sub>	HC=CHMe
Gu	124	138	152	150	164
Sy	154	168	182	180	194

# Analytical flash pyrolysis – Bio-char



**Investigation of the bio-availability of bio-char revealed that in the order 10 % of the carbon may be released as CO<sub>2</sub> in approximately 100 days when bio-char is applied to soils.**

**Classical chemical methods indicate high concentrations of glucan in the bio-char, e.g. 10 - 2 % decomposing by a first order kinetics.**

## Conclusion

**New methods for characterization of bio-char/bio-oil system have been developed:**

- ✓ **Simulation of bio-oil composition by process-near methods**
- ✓ **Determination the origin of specific compound classes found in the bio-oil**
- ✓ **Determination of residual organic compound classes in bio-char**

# Acknowledgements

## Isotope study:

**Jesper Ahrenfeldt  
Ulrik B. Henriksen  
Hanne Wojtaszewski**

## Bio-char:

**Esben W. Bruun  
Henrik Hauggaard-Nielsen  
Per Ambus  
Hanne Wojtaszewski**

**Niels Bech  
Norazana Ibrahim,  
Peter A. Jensen**