**FINNISH–JAPANESE WORKSHOP ON FUNCTIONAL MATERIALS**
**May25ー26, 2009 （Espoo and Helsinki, Finland）**

# Materials from wooden biomass

# Pyrolytic conversion of structured alkaline lignins to porous carbonized materials

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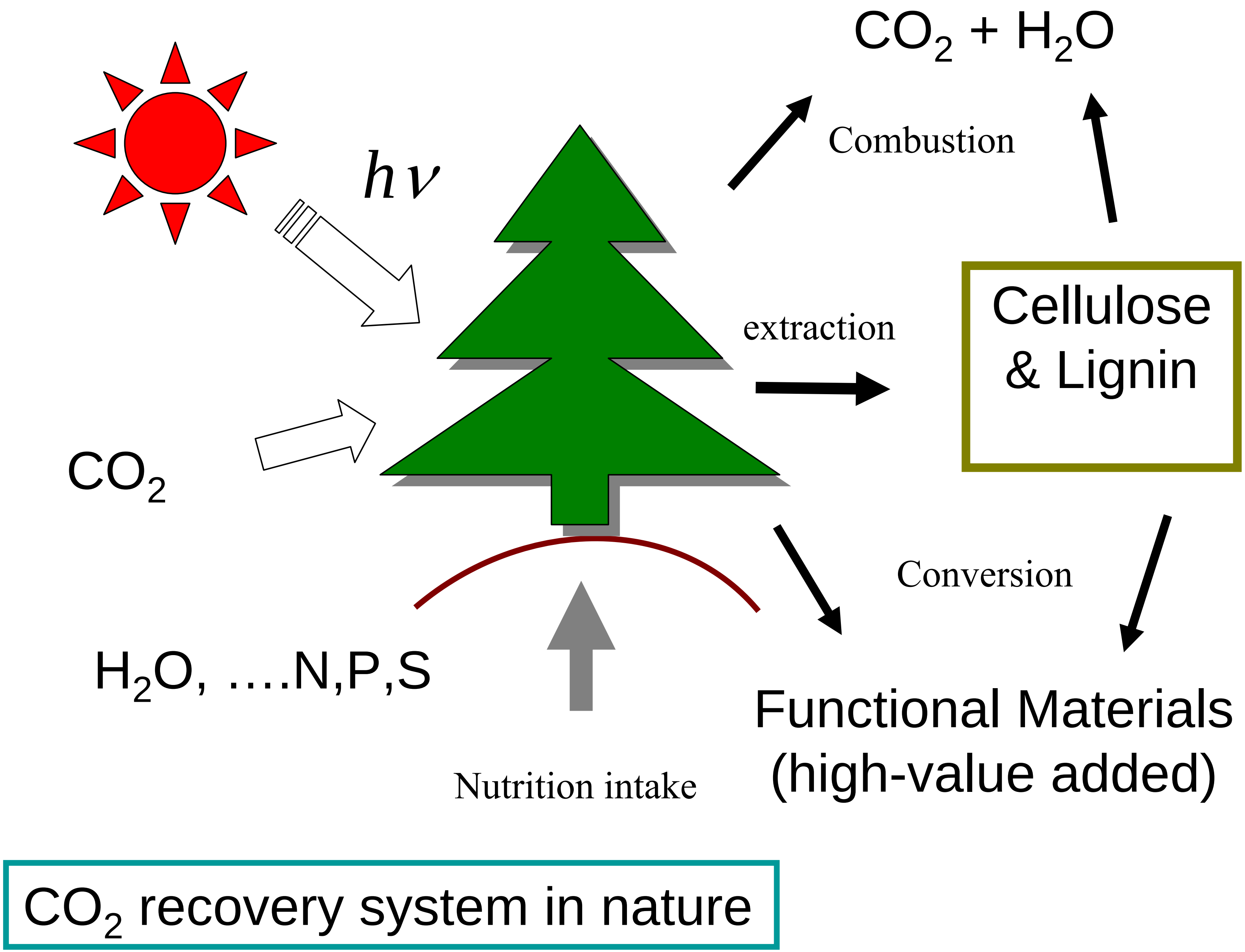
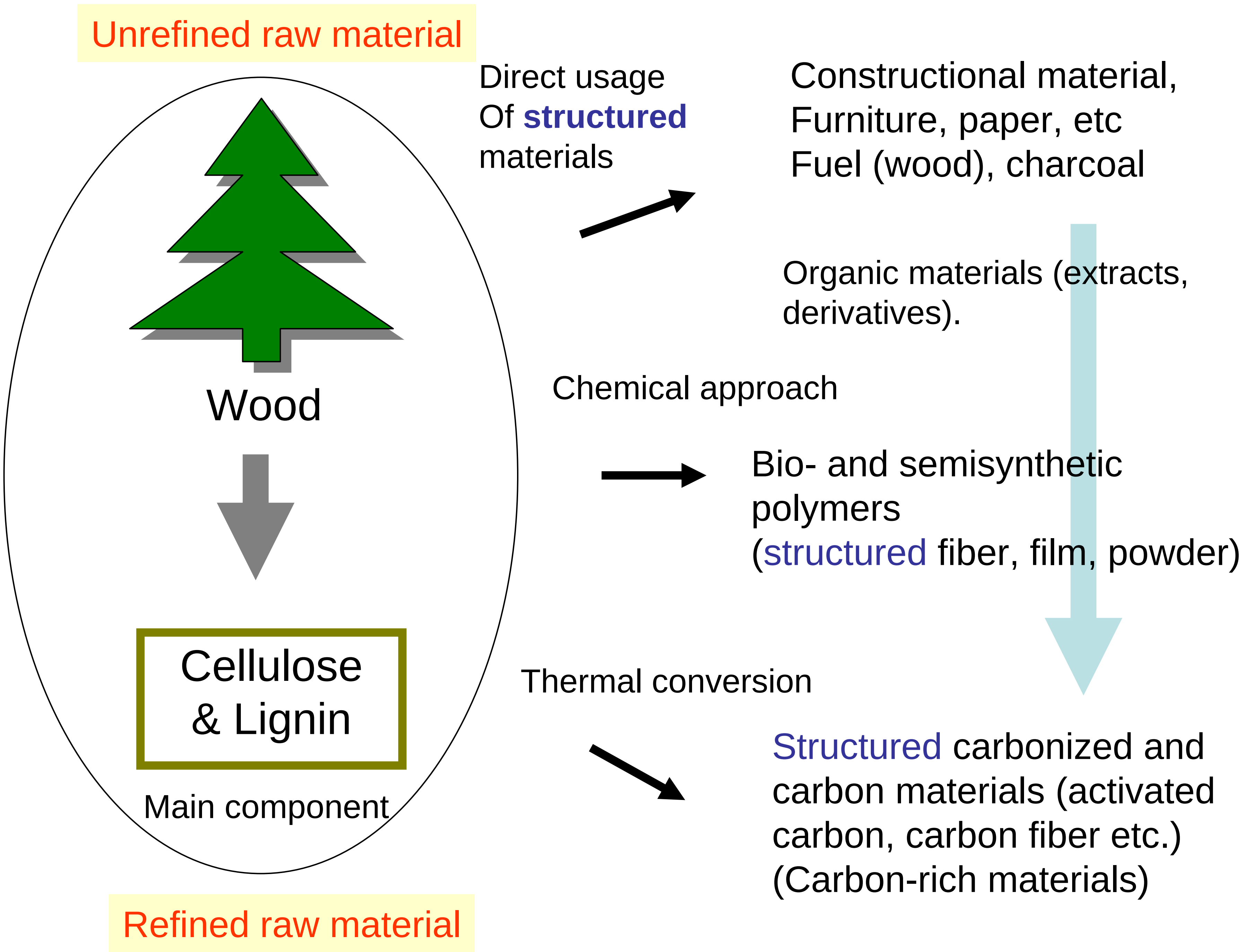


$CO_2 + H_2O$
Combustion
$h\nu$
extraction
Cellulose & Lignin
$CO_2$
Conversion
$H_2O$, ….N,P,S
Functional Materials (high-value added)
Nutrition intake
$CO_2$ recovery system in nature


Unrefined raw material
Wood
Cellulose & Lignin
Main component
Refined raw material
Direct usage Of **structured** materials
Constructional material, Furniture, paper, etc Fuel (wood), charcoal
Organic materials (extracts, derivatives).
Chemical approach
Bio- and semisynthetic polymers (structured fiber, film, powder)
Thermal conversion
Structured carbonized and carbon materials (activated carbon, carbon fiber etc.) (Carbon-rich materials)

## Purpose of our research

# Synthesis of functional carbon-rich materials from wooden biomass

Organic materials $\xrightarrow{\Delta}$ Semiconducting materials $\xrightarrow{\Delta}$ Conducting carbonized materials $\xrightarrow{\Delta}$ Carbon materials

300ºC ⟷ 800ºC ⟷ 1500ºC

Cellulose
& Lignin

Low content of C
Various functional groups in the material

**Possible to restructurize**

→

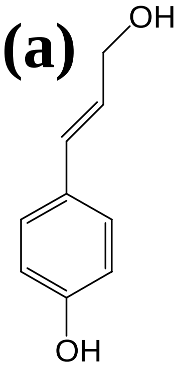
Structured C-rich Materials
High-C content: uniform & homogeneous composition

Application: thermoelectric-conversion, Photovoltaic & sollar cells, electrodes for batteries, fuel cell, EDLC, Stable porous Energy-source ($H_2$ etc) storage material etc.

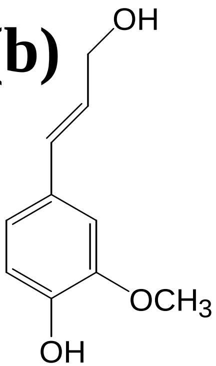
# Lignin

<aromatic structural unit>

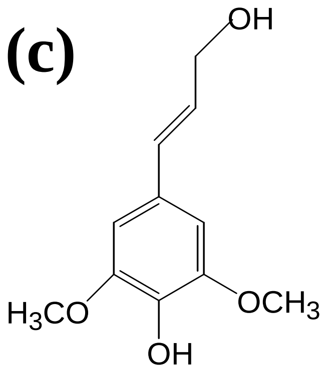
(a)




(b)

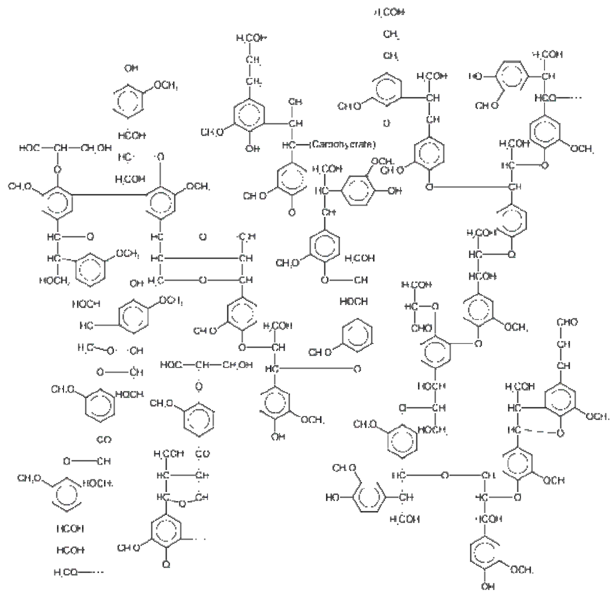



(c)




(a) *p*-coumaryl alcohol
(b) coniferyl alcohol
(c) sinapyl alcohol

<a possible structure>



**Advantage of lignin to convert into carbon materials:**
**Lignin has the phenolic components: high C fixation ability on anaerobic pyrolysis**

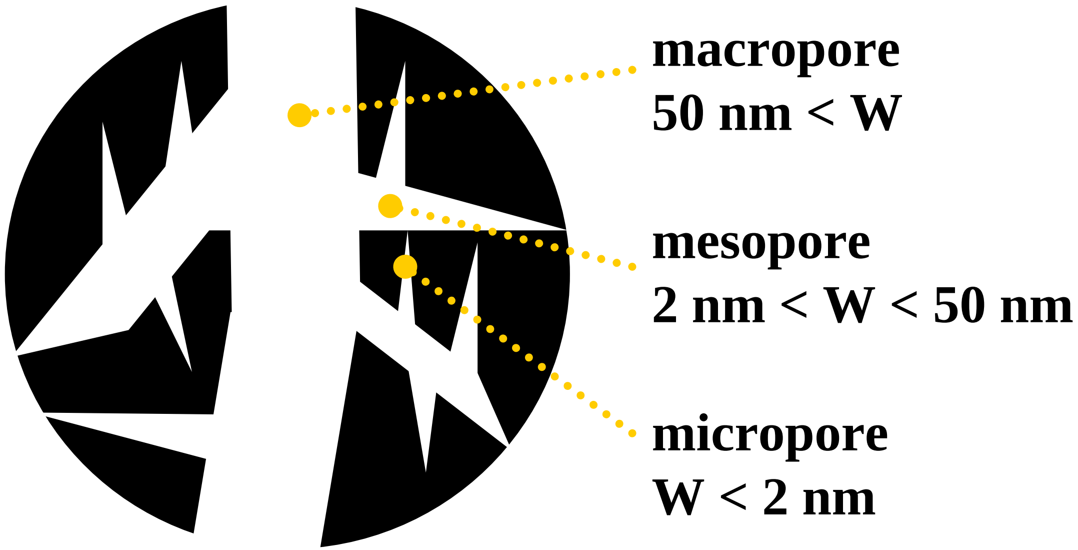
There has been reported several results on carbonization of lignin and preparation of activated carbon

# Activated carbon and the pore structure

**<characteristics>**
**Surface area : ～1000 m²/g**

**<preparation>**
**Activated carbon:Physical and chemical activation**

**<applications>**
**Adsorbent & gas sotrage**
**molecular sieve**
**electrodes**

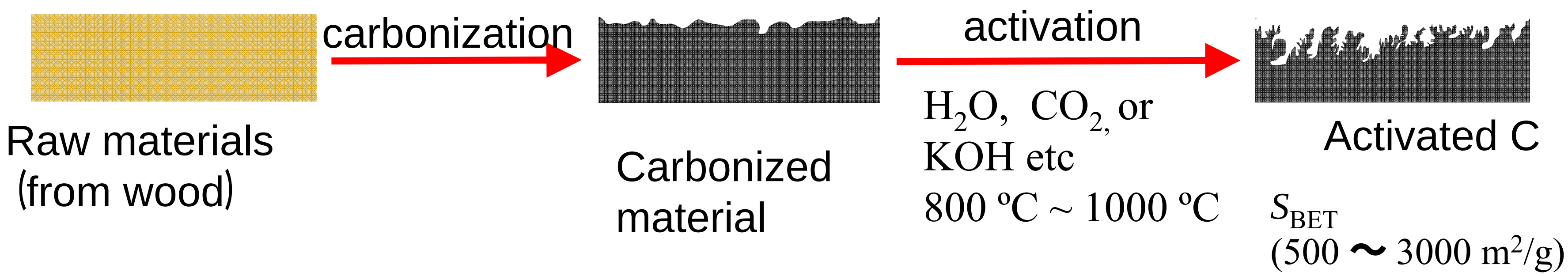



**micropore**
↓
**Surface area**
**(adsorption site)**

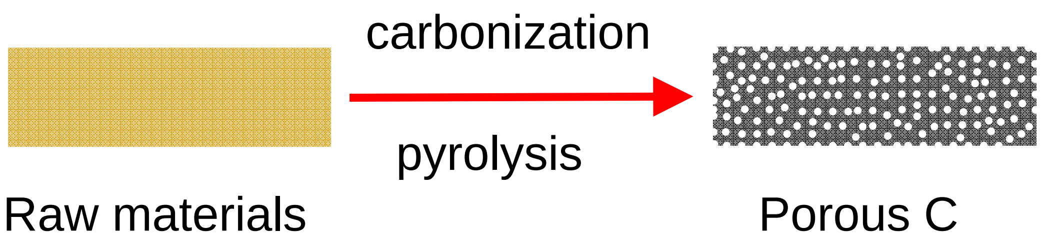
**Meso,macropore**
↓
**pore volume**
**(diffusion of material)**

# Preparation methods of porous carbon

## <Activated method> conventional




## <Pyrolytic method>




Without activation process

Porosity is largely dependent on the hardening and elimination temperatures of raw mateials

① Pyrolysis of alkaline lignin

# Alkaline Lignin

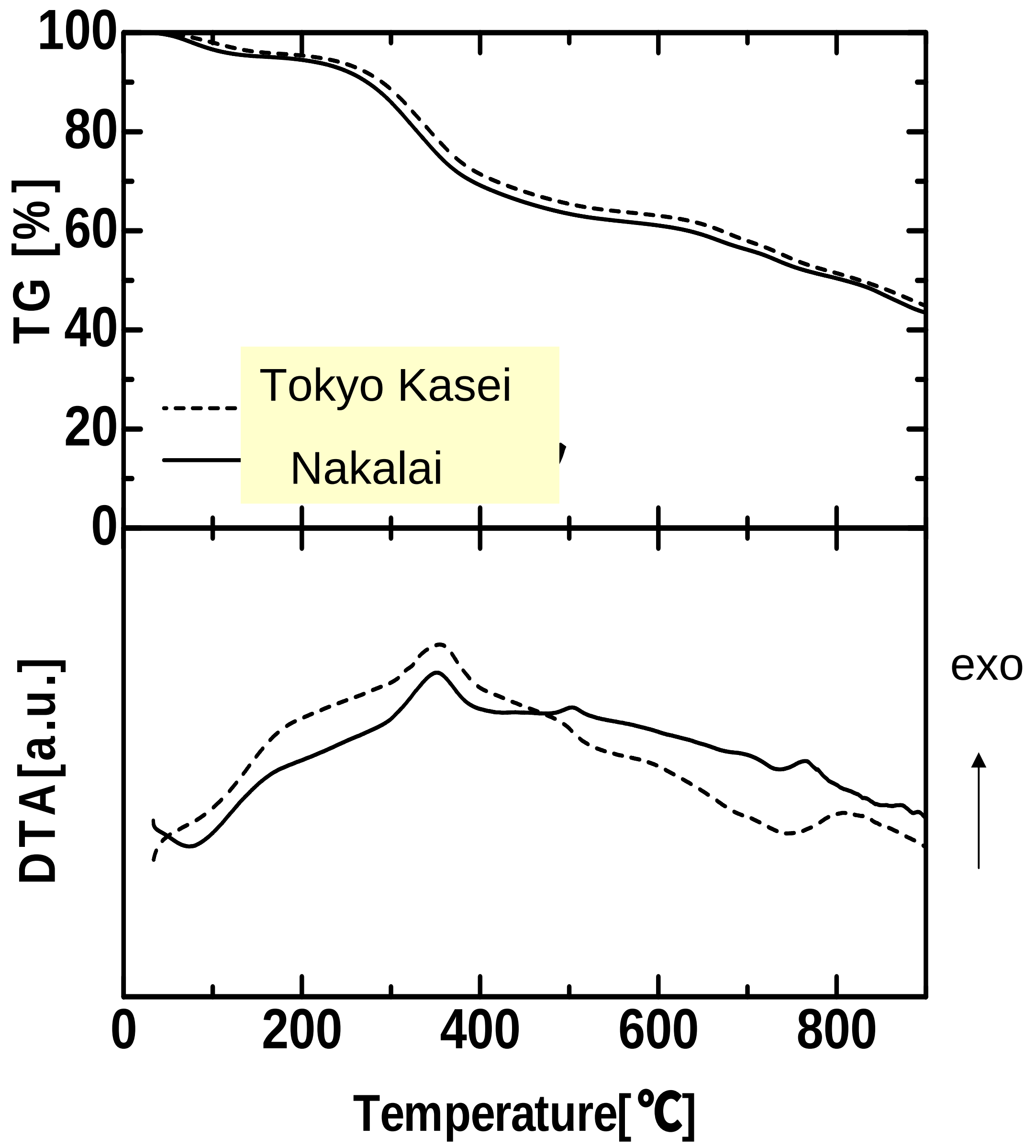
Black powder, Water soluble

Elemental analysis

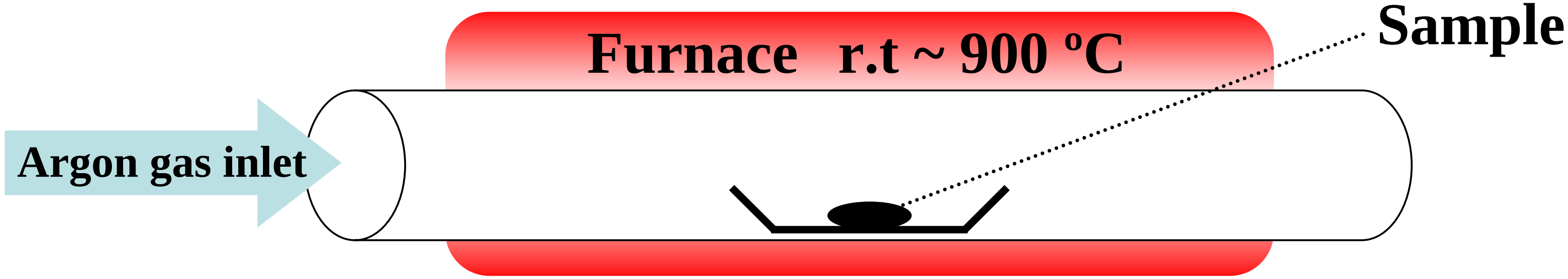
C: 51.72 %, H: 5.12 %, N: 0.13 % (Nacalai),

C: 51.83 %, H: 4.78 %, N: 0.11 % (Tokyo Kasei)

Reagent grade(available)



## ① Carbonization of alkaline lignin




### Carbonization conditions

(annealing time)

CL1: r.t ~ 900 °C 10 °C/min

CL2: r.t ~ 900 °C 4 °C/min

CL3: r.t ~ 900 °C 2 °C/min

CL4: r.t ~ 900 °C 1 °C/min

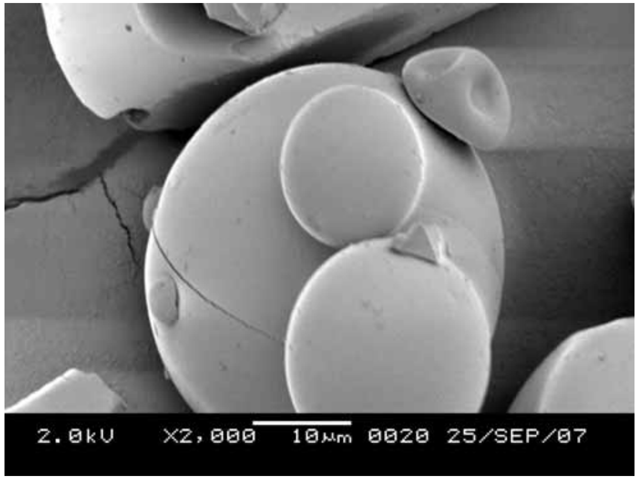
CL5: r.t ~ 300 °C 10 °C/min 300 °C (1) 300 °C ~ 900 °C 10 °C/min

CL6: r.t ~ 350 °C 10 °C/min 350 °C (1) 350 °C ~ 900 °C 10 °C/min

CL7: r.t ~ 350 °C 10 °C/min 350 °C (2) 350 °C ~ 900 °C 10 °C/min

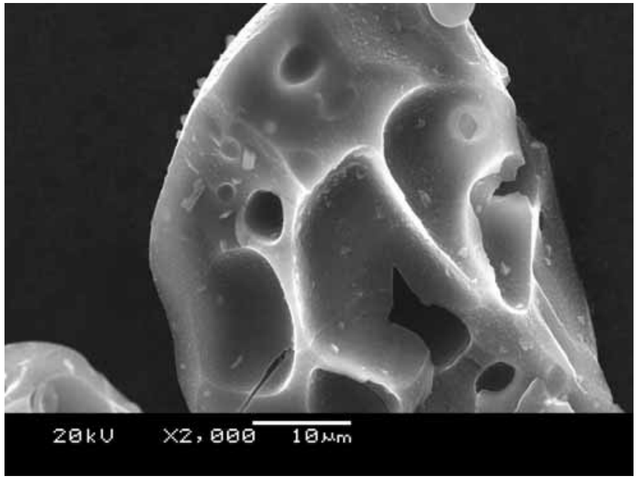
CL8: r.t ~ 350 °C 10 °C/min 350 °C (3) 350 °C ~ 900 °C 10 °C/min

# SEM



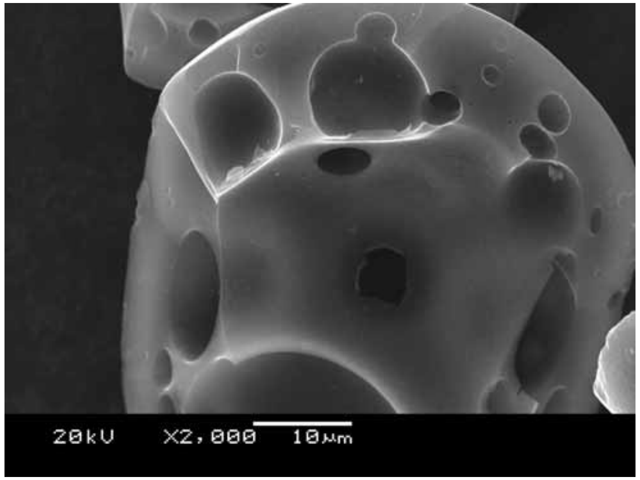

10 μm

Alkaline lignin




10 μm

**CL4**




10 μm

**CLW**

**CL4**：deposition on the surface was a Na salt confirmed by XPS

**CLW**： After washing **CL4** with water, the deposition was cleaned off

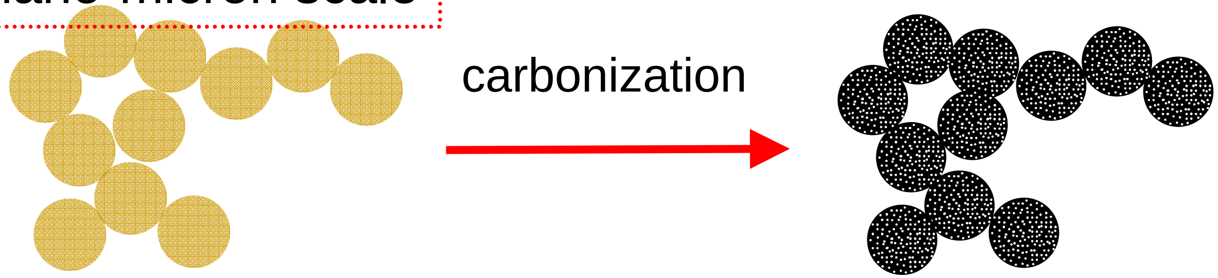
Carbonization results and $N_2$ adsorption data

| sample | Yield (%) | $S_{BET}$ ($m^2/g$) | $\alpha_s$ | | | $V_{total}$ (ml/g) | DH | |
|---|---|---|---|---|---|---|---|---|
| | | | $S_{total}$ ($m^2/g$) | $V_{micro}$ (ml/g) | $W_{micro}$ (nm) | | $V_{meso}$ (ml/g) | $V_{meso}/V_{total}$ (%) |
| **CL4** | **46** | **664** | **655** | **0.09** | **0.90** | **0.55** | **0.15** | **28** |
| **CLW** | — | **899** | **1031** | **0.17** | **0.65** | **0.69** | **0.19** | **27** |

# Control of structure and morphology of carbonized materials

Particles in nano-micron scale

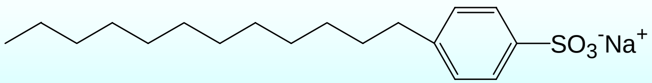
Microporous C-particles



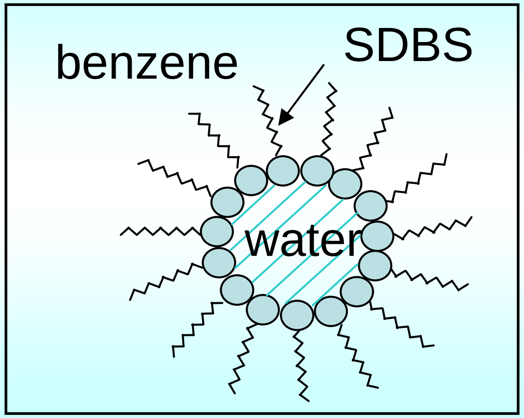

Aims: 1) Increase of effective surface area. 2) Generation of new pore space between the particles

Typical conditions

| | Water (ml) | SDBS (mg) | Benzene (ml) |
|---|---|---|---|
| ML3 | 5 | 50 | 45 |



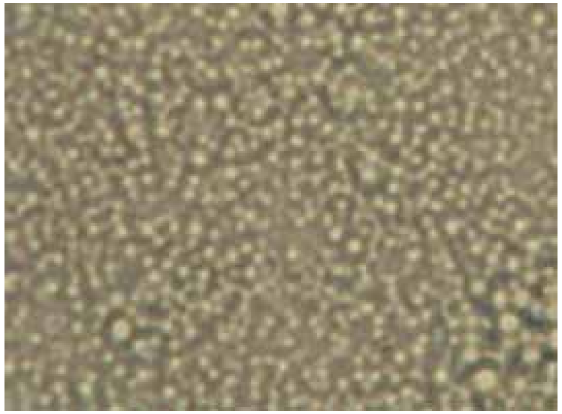

Sodium Dodecylbenzenesulfonate(SDBS)



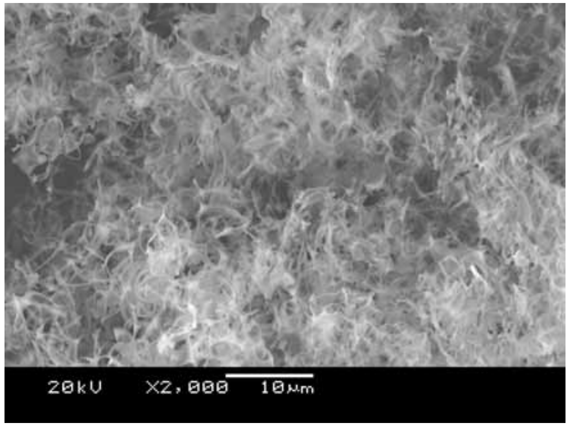

Reverse micelle

② Preparation of micellar lignins and the carbonization

# Preparation of micellar lignins (ML) and their carbonization

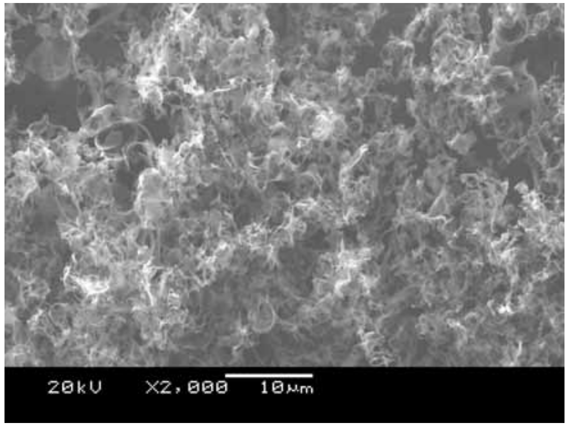


(in solution)



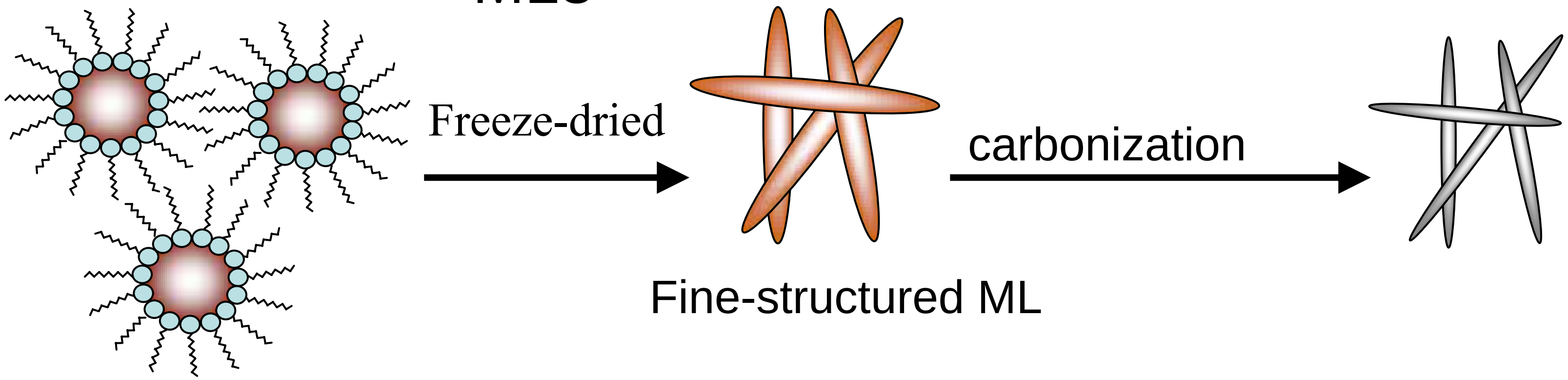

(freeze-dried)

ML3




10 μm

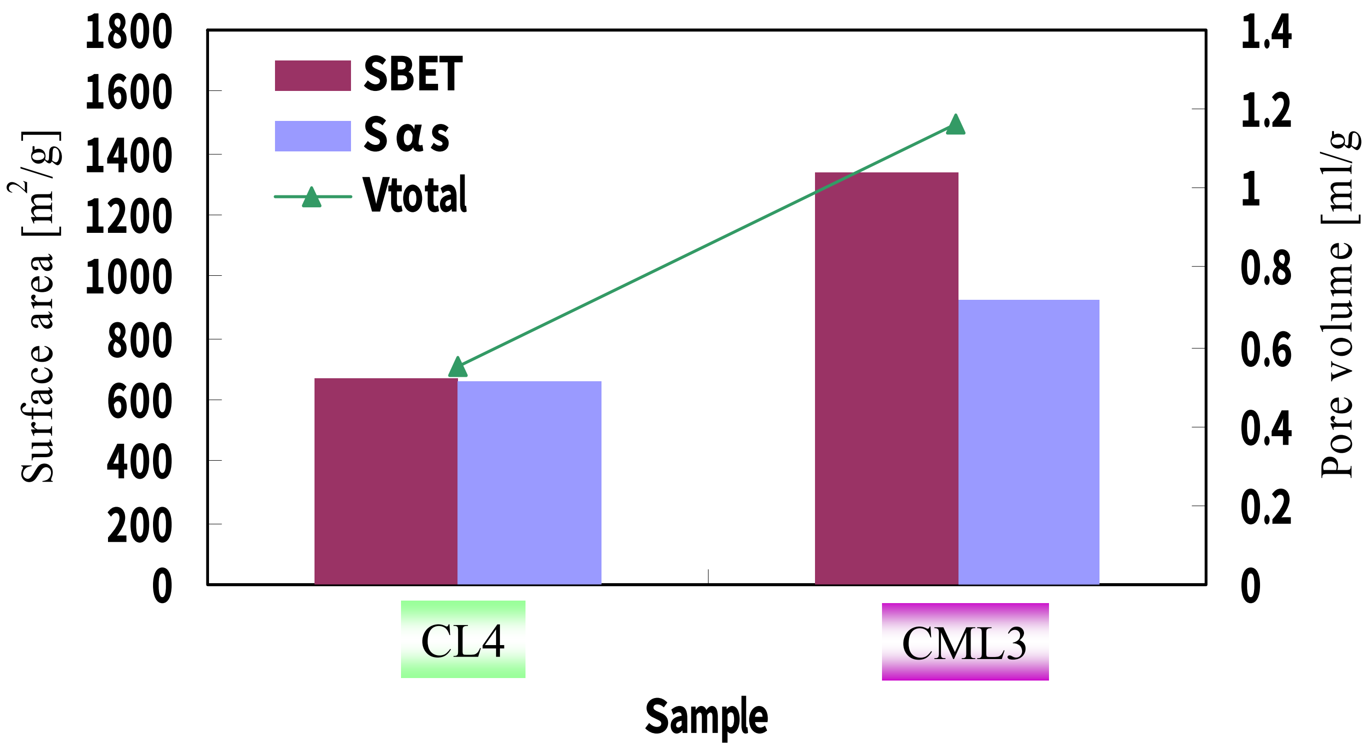
CML3




**Particle samples could not be obtained in this case.**
**In order to obtain particle lignins, (3) rigid lignin gels are synthesized**

# Comparison of $N_2$ adsorption results of CL and CML

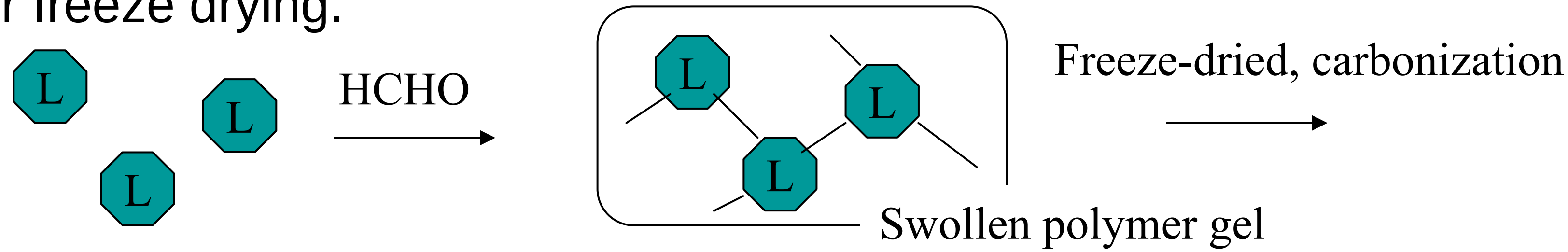
| sample | Yield (%) | $S_{BET}$ ($m^2$/g) | $\alpha_s$ $S_{total}$ ($m^2$/g) | $\alpha_s$ $V_{micro}$ (ml/g) | $\alpha_s$ $W_{micro}$ (nm) | $V_{total}$ (ml/g) | DH $V_{meso}$ (ml/g) | DH $V_{meso}$/ $V_{total}$ (%) |
|---|---|---|---|---|---|---|---|---|
| CL4 | 46 | 664 | 655 | 0.09 | 0.90 | 0.55 | 0.15 | 28 |
| CML3 | **17** | **1340** | **928** | 0.19 | 1.14 | **1.16** | 0.45 | 39 |



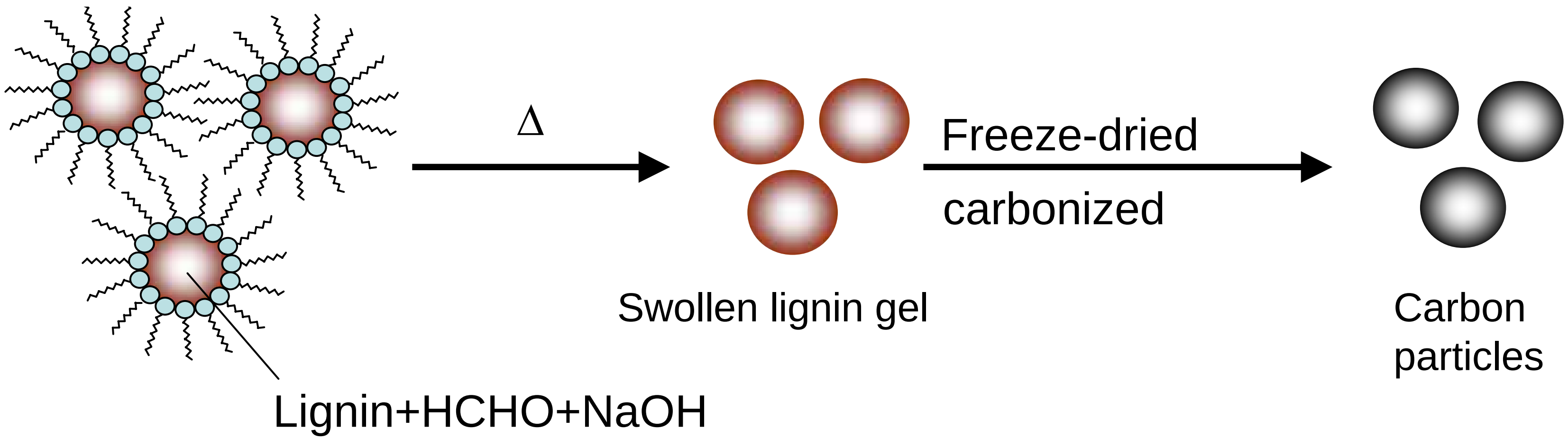
# Toward synthesis of carbonized lignin particles

## ③ Preparation of alkaline lignin gel and the carbonization

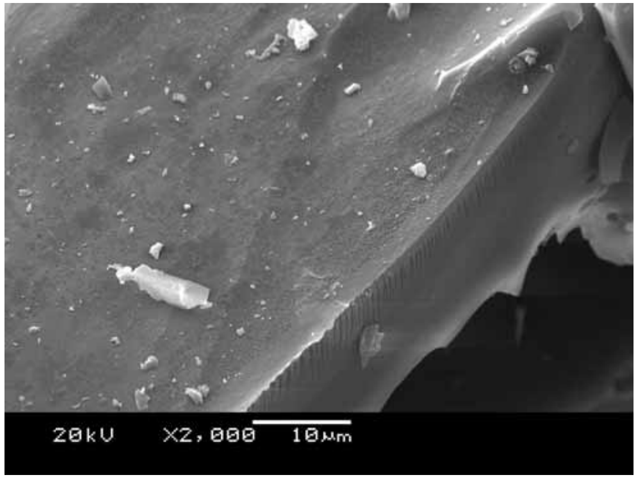
Under basic aqueous conditions, alkaline lignin was reacted with formaldehyde to give a swelled polymer gel, which was carbonized after freeze drying.



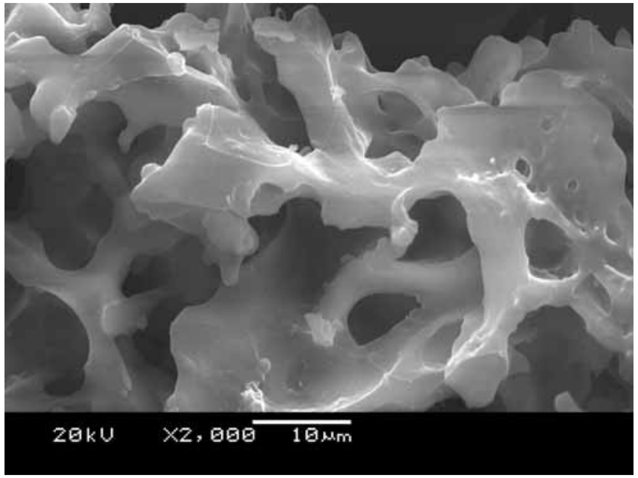

## ④ Preparation of lignin-gel particles and their carbonization



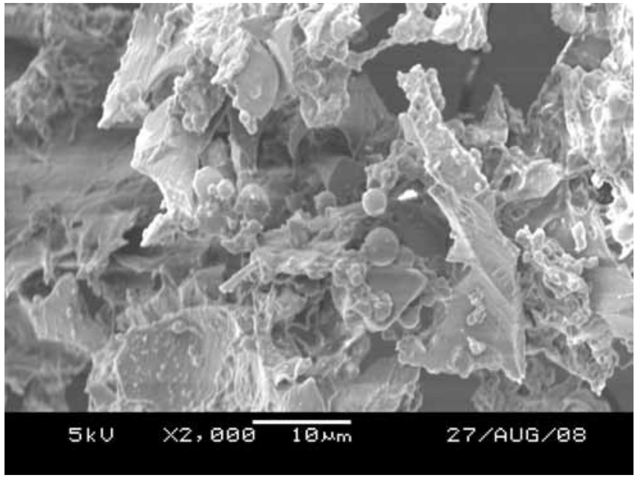
# SEM Images of lignin deriv. before and after carbonization



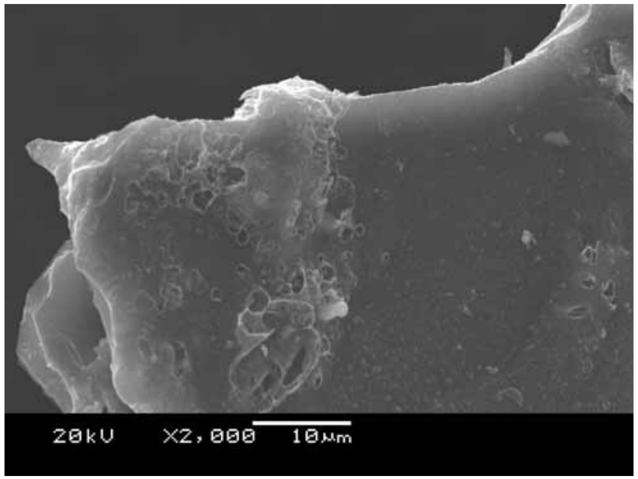

10 μm
**LG**



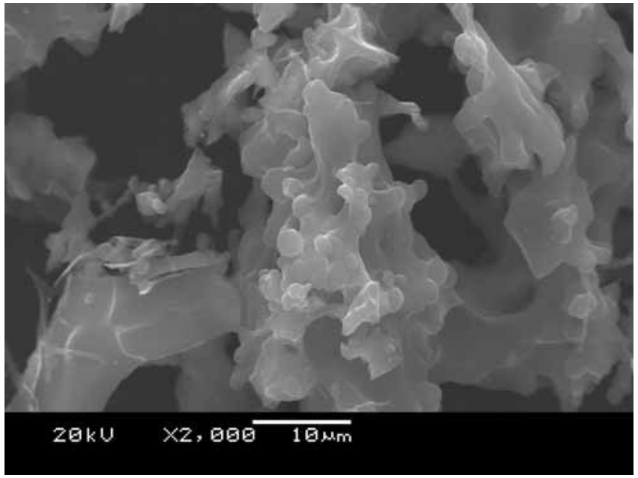

10 μm
**MLG1**



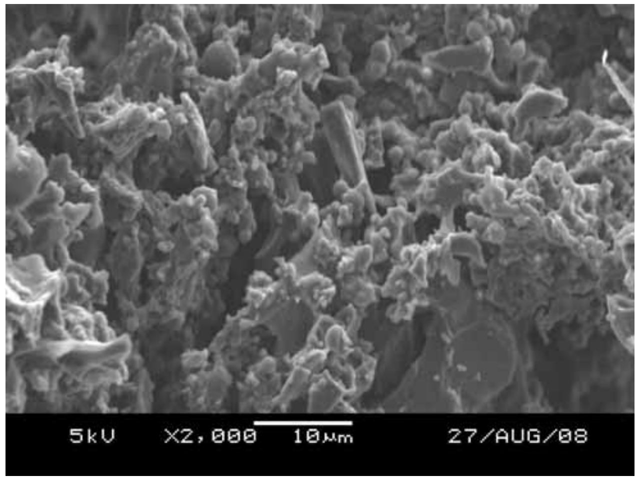

10 μm
**MLG2**




10 μm
**CLG**



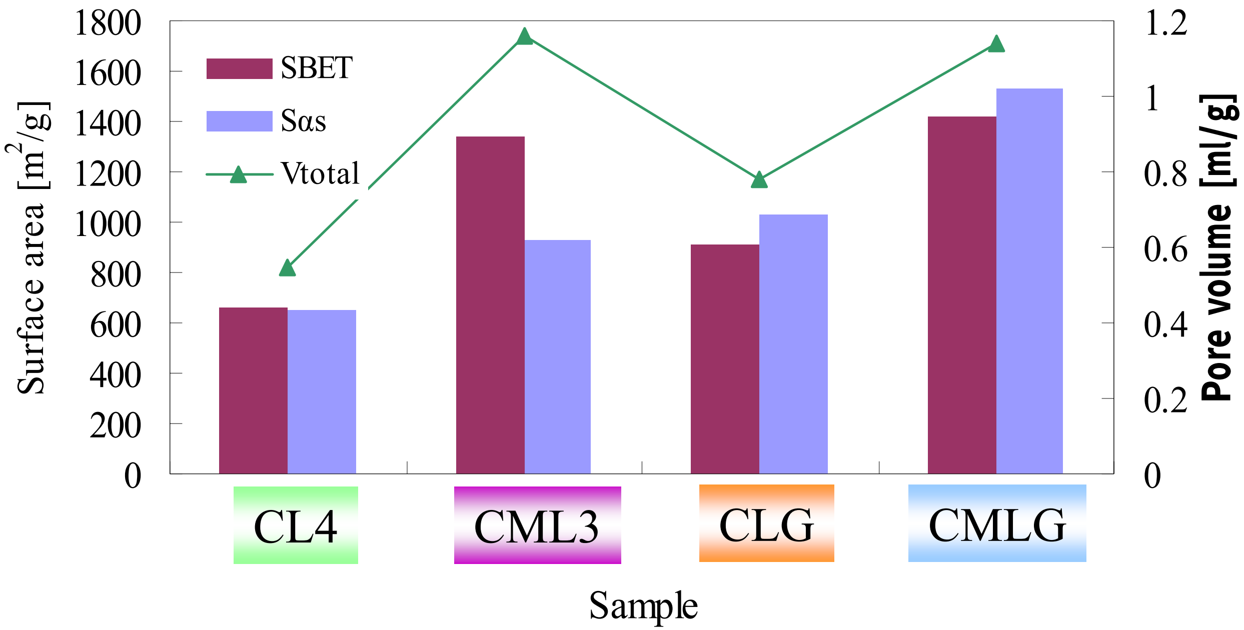

10 μm
**CMLG1**




10 μm
**CMLG2**

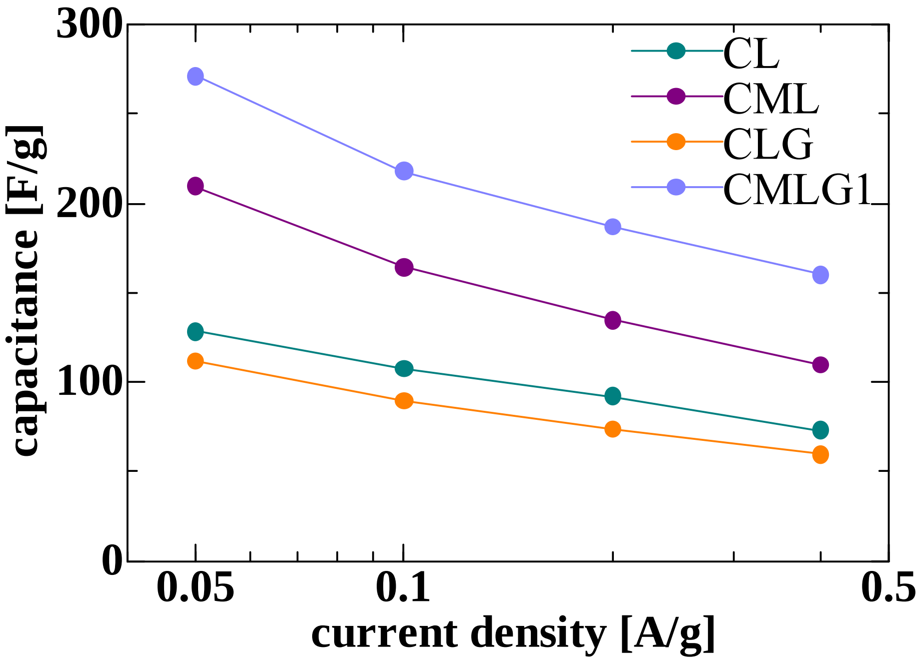
# Carbonization and $N_2$ adsorption results

| sample | Yield (%) | $S_{BET}$ ($m^2/g$) | $\alpha_s$ | | | $V_{total}$ (ml/g) | DH | |
|---|---|---|---|---|---|---|---|---|
| | | | $S_{total}$ ($m^2/g$) | $V_{micro}$ (ml/g) | $W_{micro}$ (nm) | | $V_{meso}$ (ml/g) | $V_{meso}/V_{total}$ (%) |
| CL4 | 45 | 738 | 920 | 0.26 | 0.70 | 0.50 | 0.06 | 11 |
| CML3 | 17 | 1340 | 928 | 0.19 | 1.14 | 1.16 | 0.45 | 39 |
| CLG | 42 | 915 | 1029 | 0.17 | 0.70 | 0.78 | 0.23 | 30 |
| CMLG | 29 | **1423** | **1528** | 0.28 | 0.78 | **1.14** | 0.30 | 26 |



# Electrical double layer capacitor (EDLC) characteristics of the carbonized lignins

**1M $H_2SO_4$**




**0.5M $Et_4NBF_4$/ PC**

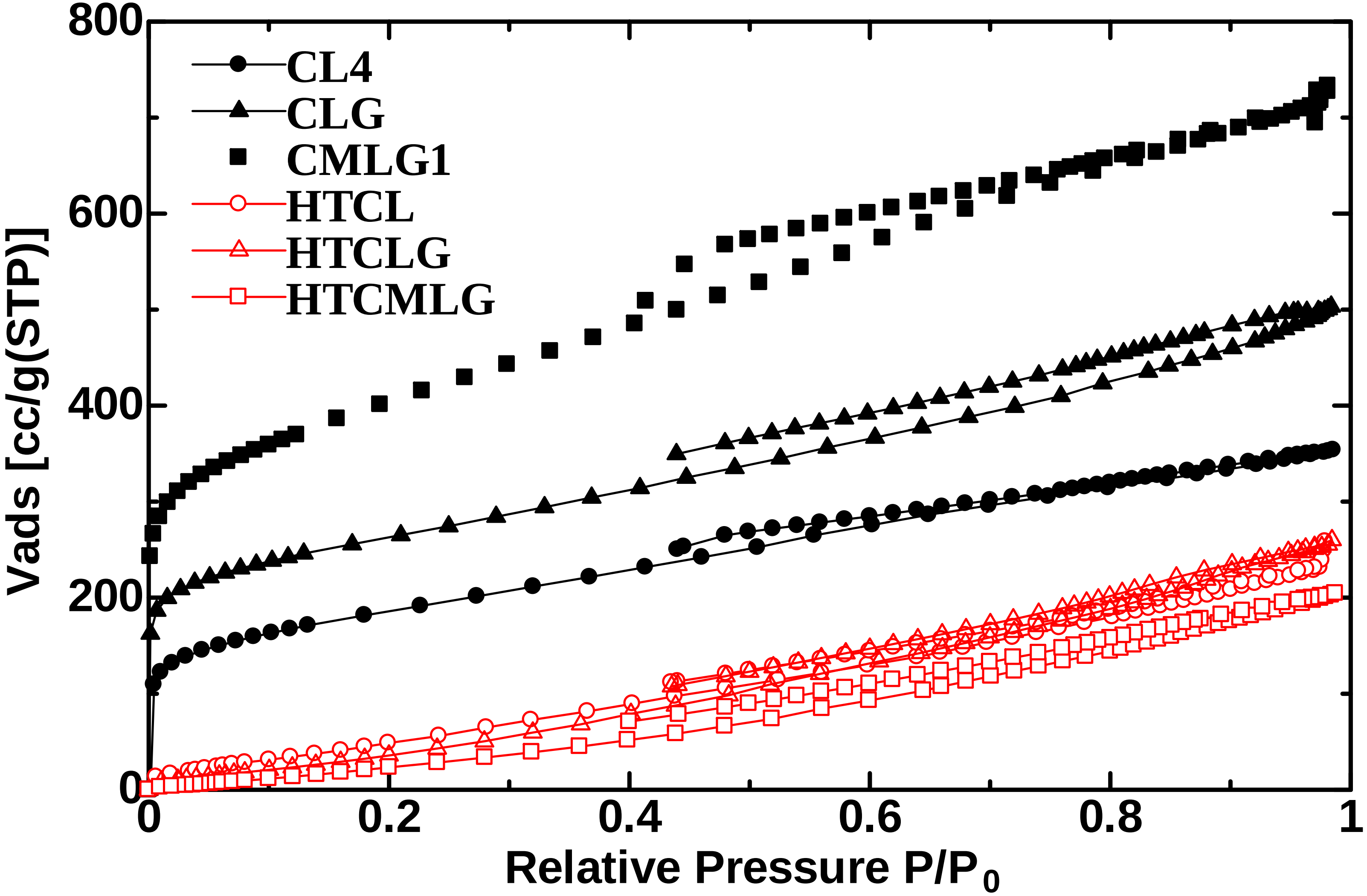
| Sample | Anion (F/g) 0 ~ + 1.5V | Cation (F/g) 0 ~ -1.5V |
|---|---|---|
| CL | 11 | 7 |
| CML | 85 | 55 |
| CLG | 41 | 23 |
| CMLG1 | 60 | 53 |

at 0.05 A/g

$Et_4N^+$ : 0.68nm

$BF_4^-$ : 0.44nm

# Effect of heat-treatment (1500℃) on porosity of the carbonized lignins



| Sample | $S_{BET}$ (m$^2$/g) | $\alpha_s$ | | | $V_{total}$ (ml/g) | DH | |
|---|---|---|---|---|---|---|---|
| | | $S_{total}$ (m$^2$/g) | $V_{micro}$ (ml/g) | $W_{micro}$ (nm) | | $V_{meso}$ (ml/g) | $V_{meso}/V_{total}$ (%) |
| HTCL | **213** | - | - | - | **0.40** | **0.18** | 45 |
| HTCML | - | - | - | - | - | - | - |
| HTCLG | **176** | - | - | - | **0.40** | **0.22** | 55 |
| HTCMLG | **187** | - | - | - | **0.32** | **0.20** | 63 |
| CL4 | 664 | 655 | 0.09 | 0.90 | 0.55 | 0.15 | 28 |
| CML3 | 1340 | 928 | 0.19 | 1.14 | 1.16 | 0.45 | 39 |
| CLG | 915 | 1029 | 0.17 | 0.70 | 0.78 | 0.23 | 30 |
| CMLG1 | 1423 | 1528 | 0.28 | 0.78 | 1.14 | 0.30 | 26 |

# Summary & Conclusions

Porous carbons are obtained from alkaline lignin (L) and their structured derivatives (ML, LG, MLG) by pyrolytic method.

Surface area and microporosity of CL can be increased by the structuration of the starting materials (ML, LG, MLG). Meso to macroporous spaces (pore volume) can be enlarged by the structuration.

Microporosity can be eliminated from the carbonized lignins by 1500ºC heat-treatment.

During the carbonization and heat-treatment processes, these materials almost retain their surface morphology.

These thermal conversion reactions are going to be applied to other lignin and cellulose derivatives in various forms (particle, film and fiber).

**Aims and key words of this research** : Conversions of wooden biomass to semiconductive and conductive carbon-rich materials; Addition of high carbon fixation ability; Regulation of nano-structures (porosity etc); Applications

*Acknowledgement: Thanks to T. Hirukawa (Univ Tsukuba) & T. Hata (Kyoto Univ)*