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Biorefinica Conference Workshop
Osnabruck, Germany

Recent Progress in Biorefineries as Introduced by Supercritical Fluid Science and Technology

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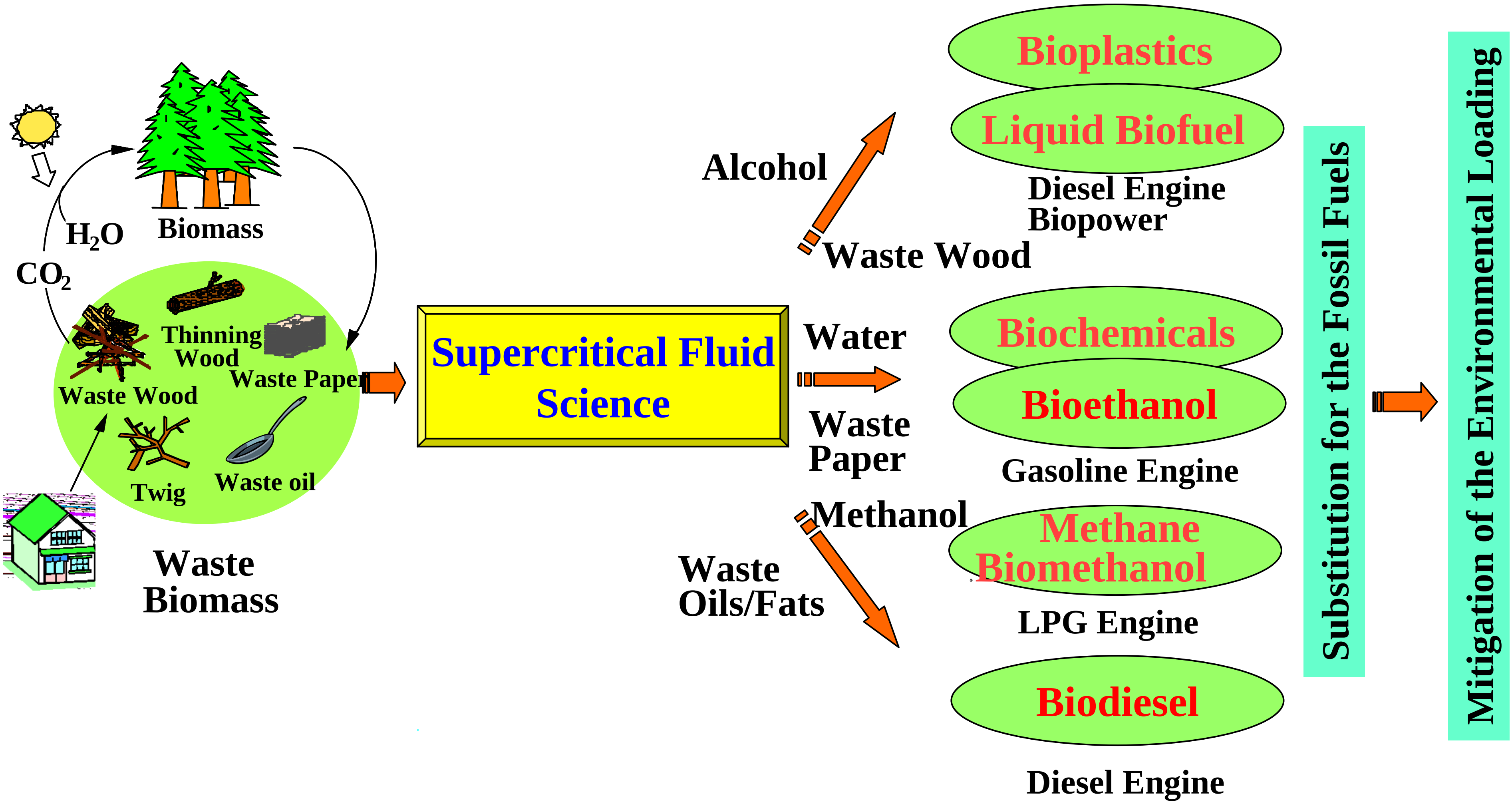
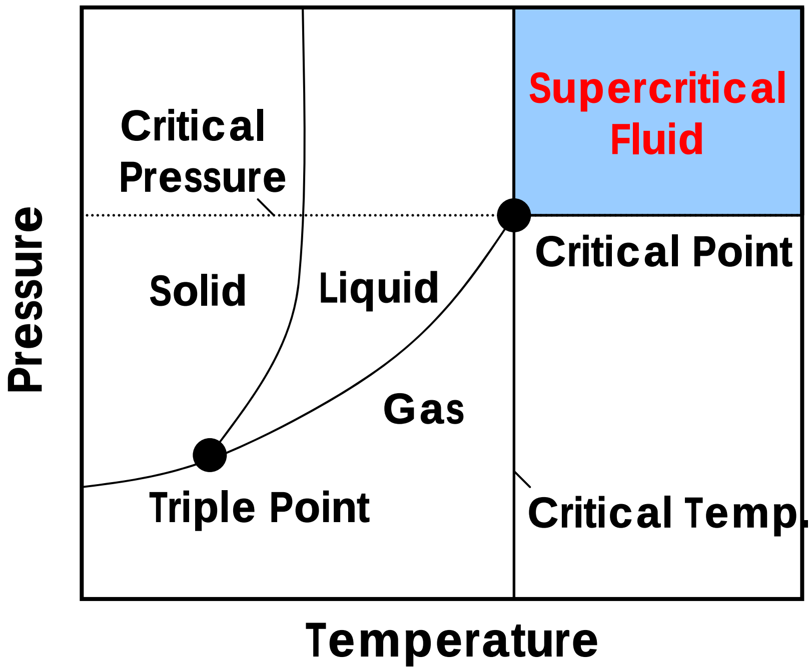
Biorefinery from Biomass by Supercritical Fluid Technologies



Supercritical Fluid

A pure substance may be changed into 3 phases such as gas, liquid and solid. Among these, the critical point exists between the gas and liquid.

Above the critical point, there exists the high-density fluid which cannot be condensed any more, even if temperature and/or pressure are increased. Such a substance is called "supercritical fluid".



Temperature-Pressure relation of the Pure Substance

.H_2O
Critical Point: 374., 22.1MPa

.MeOH
Critical Point: 239., 8.09MPa

Under SC condition,
.Ionic Products: Increased
(H_2O.Hydrolysis)
.Dielectric Constant: Decreased
(Hydrophilic.Hydrophobic)

Supercritical Fluid Biomass Conversion Systems

Gas-Charging Unit

Butch

Butch (Two Steps)

Continuous □Liquid-Liquid□

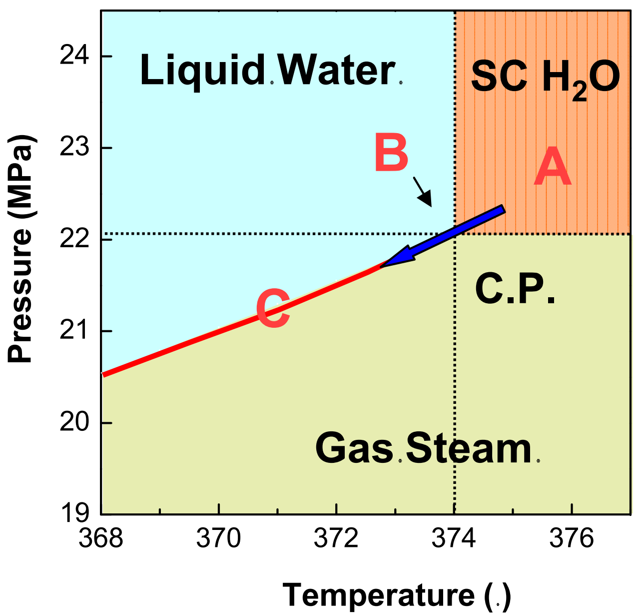
Continuous □Solid-Liquid□

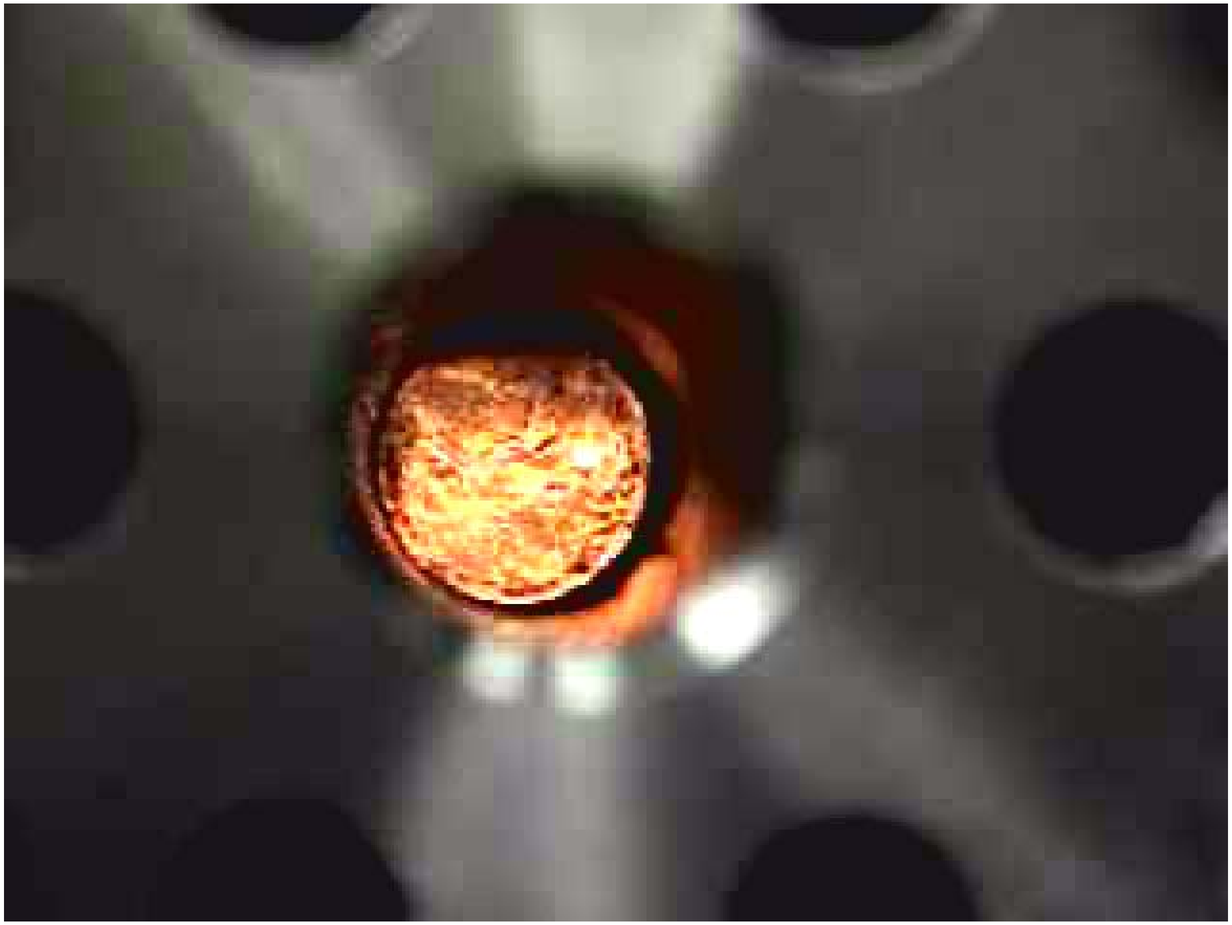
Direct Observation through Sapphire window

Pilot Plant for BDF

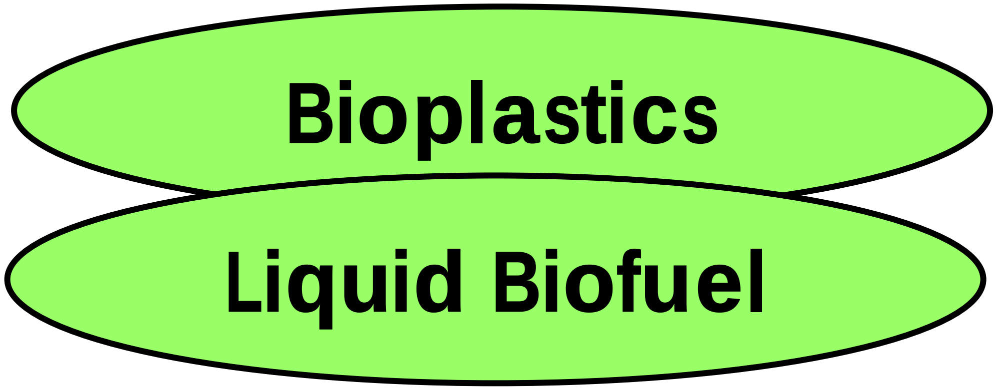
Continuous □Liquid-Liquid Two Steps□

Phase Changes of Water in a Vicinity of Its Critical Point

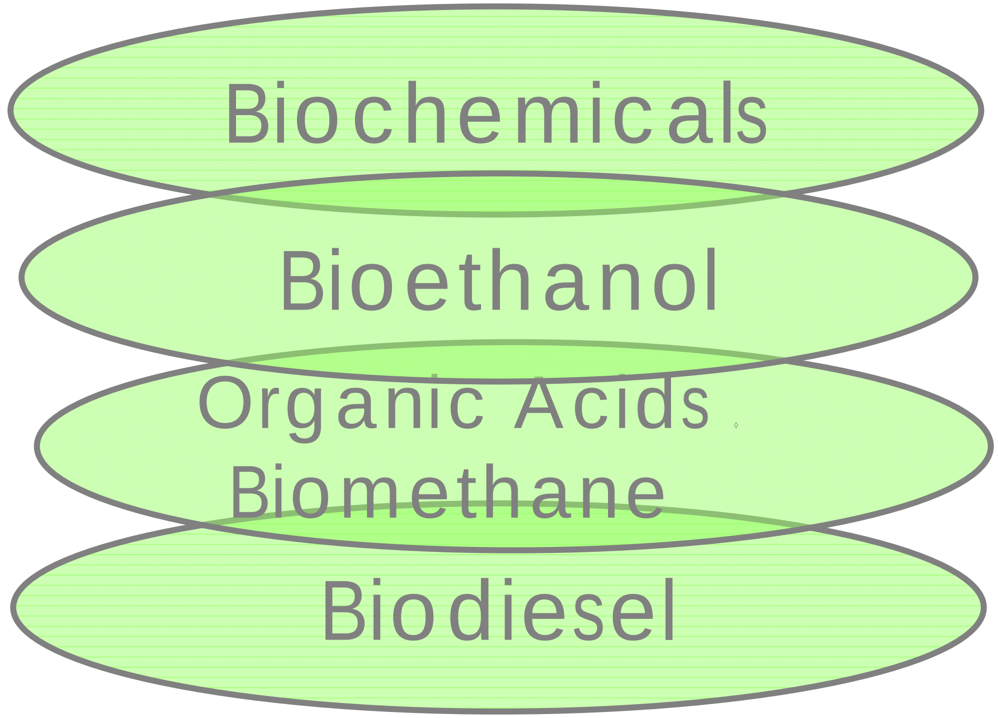




Biofuels by Supercritical Fluid Technologies



Liquefaction of Lignocellulosics by Supercritical Alcohol Technologies

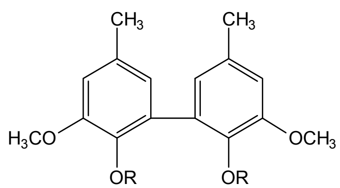
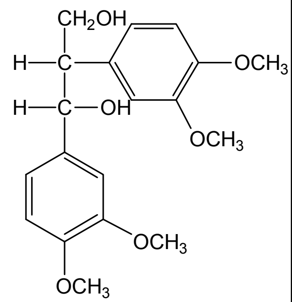
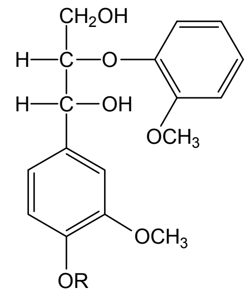
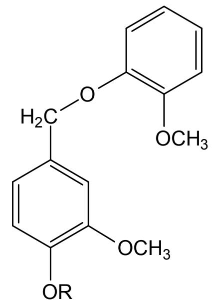


Supercritical Methanol Treatment
（350℃/43MPa）

Wood flour | **MeOH** | **MeOH-insoluble residue** | **MeOH-soluble portion**

Ref: Minami and Saka, 2003
J Wood Sci 49:73-78.

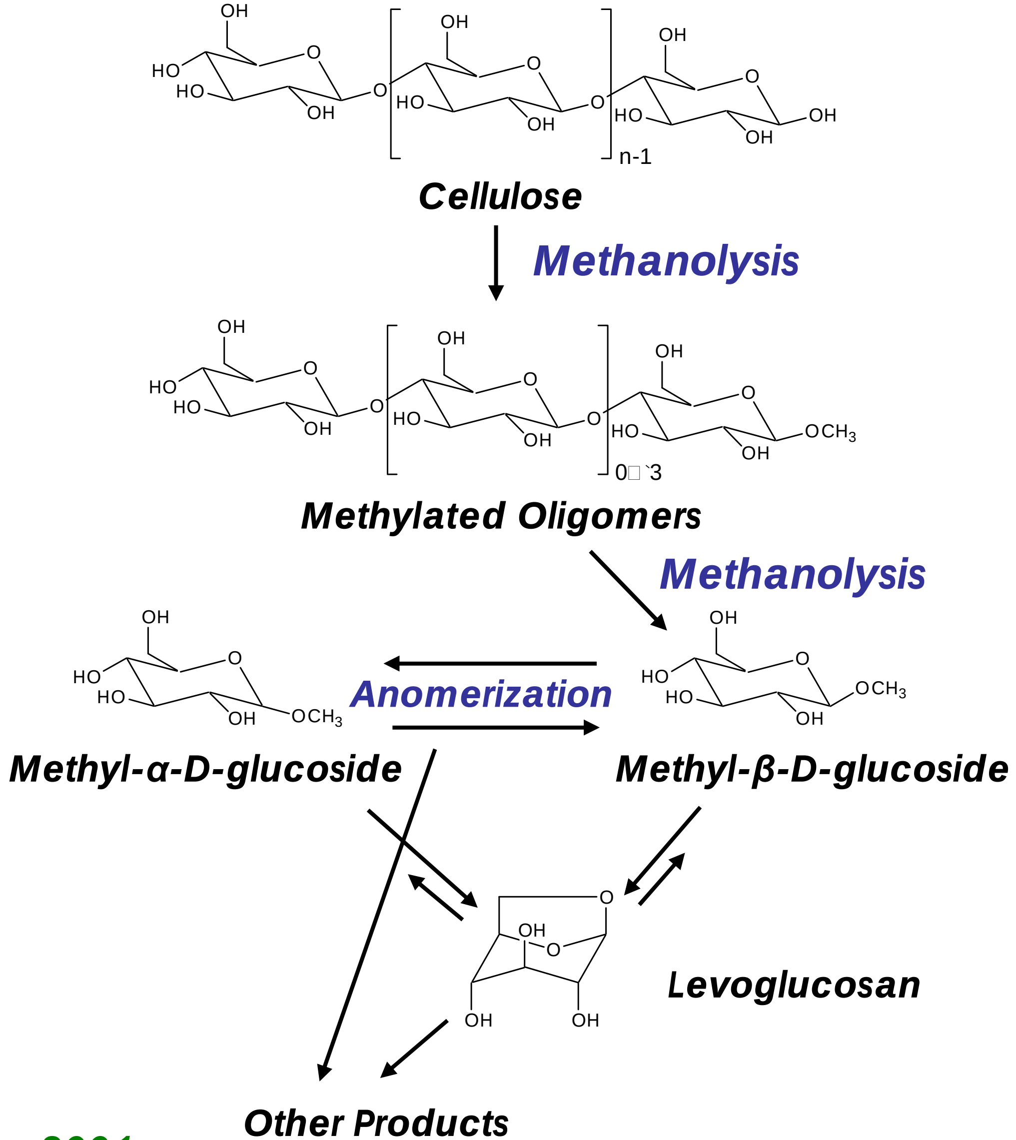
Study by Dimeric Lignin Model Compounds （270℃/27MPa）

	Condensed-Tye Linkage			Ether Linkage			
	5-5		. -1	. -*O*-4		. -*O*-4	
Structure							
	R=H	$R=CH_3$	$R=CH_3$	R=H	$R=CH_3$	R=H	$R=CH_3$
Reactivity	Very Low	Very Low	Low	High	High	Very High	High
. . 10^{-3}/sec.	.	.	.	2.8	0.34	NM	0.17
E_a . kJ/mol.	.	.	.	68.9	85.2	NM	113

N M : Difficult to evaluate due to Extremely high reactivity

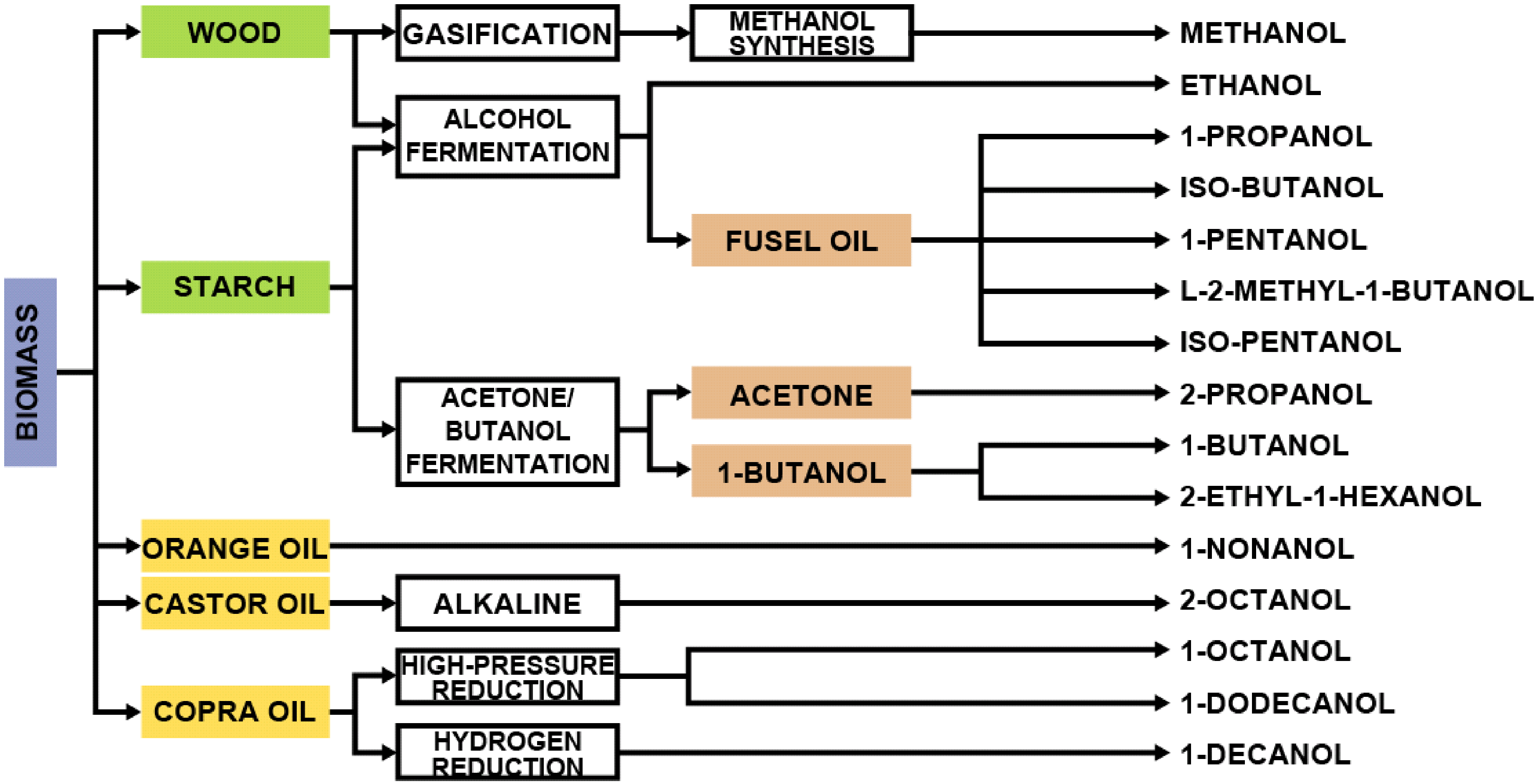
Ref: Minami et al, 2003
J Wood Sci 49:158-165.

Decomposition of Cellulose in Supercritical Methanol

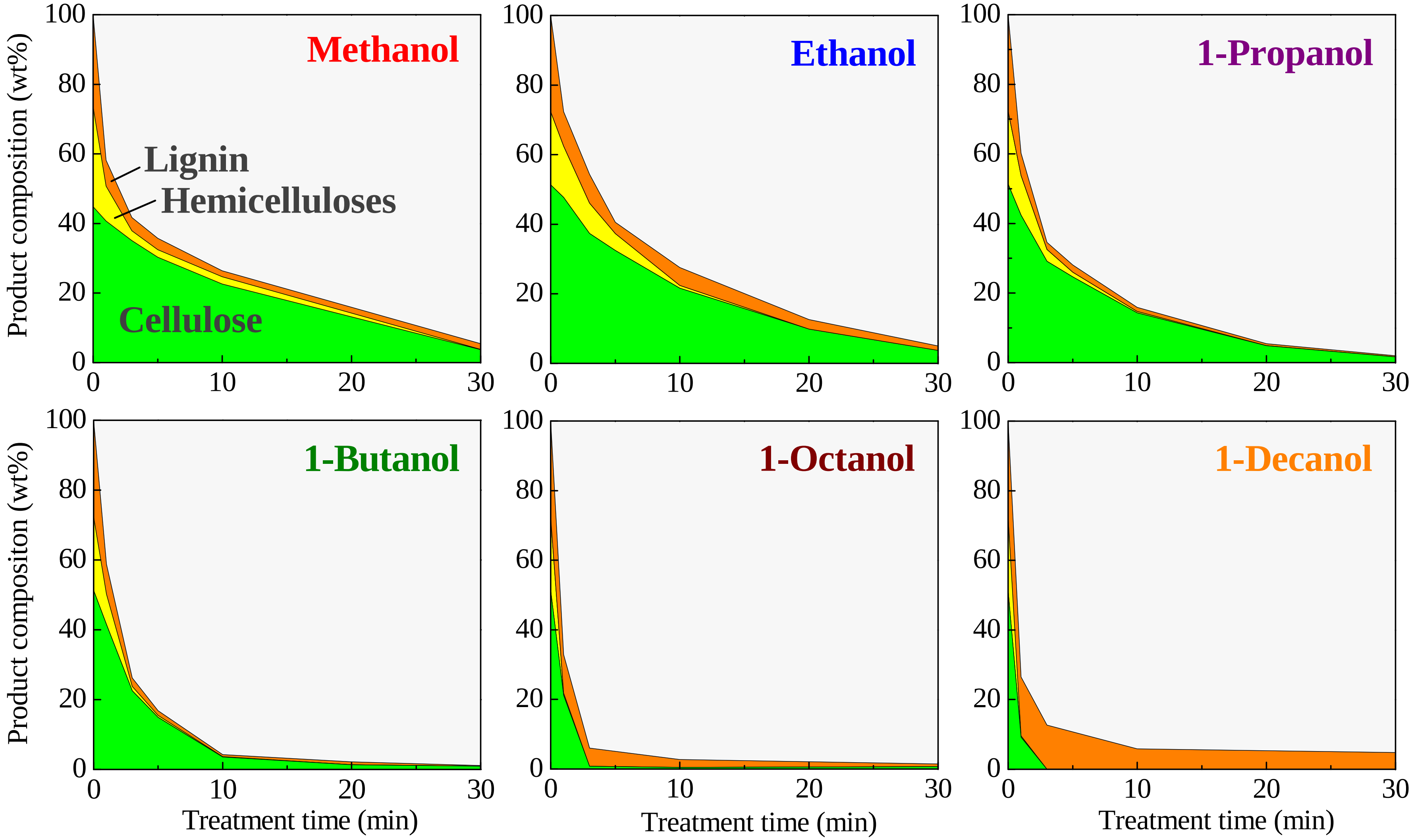


Ref: Ishikawa and Saka, 2001
Cellulose 8:189-195.

Various Alcohols Available from Biomass

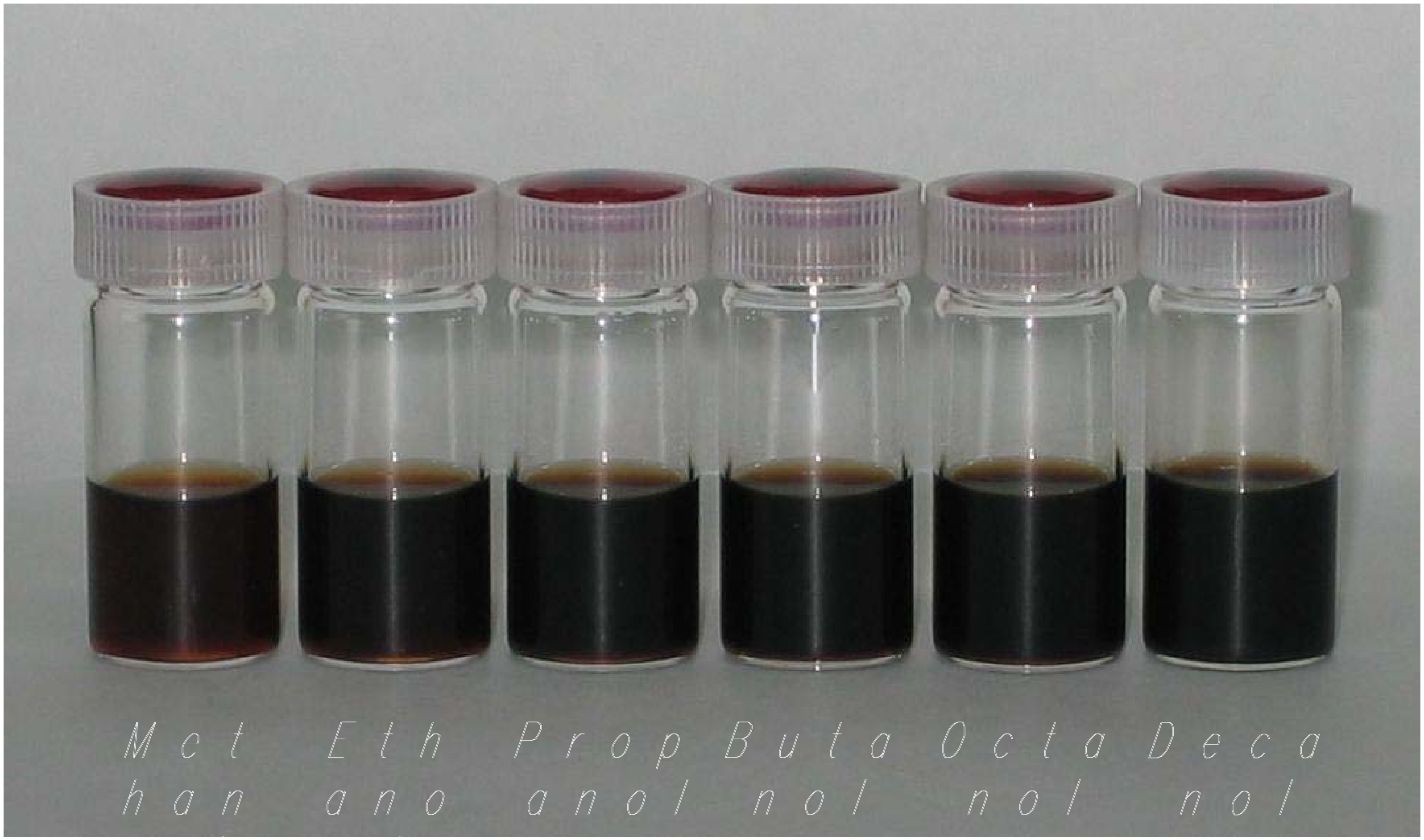


Changes in the composition of the alcohol-insoluble residue under the condition of 350°C



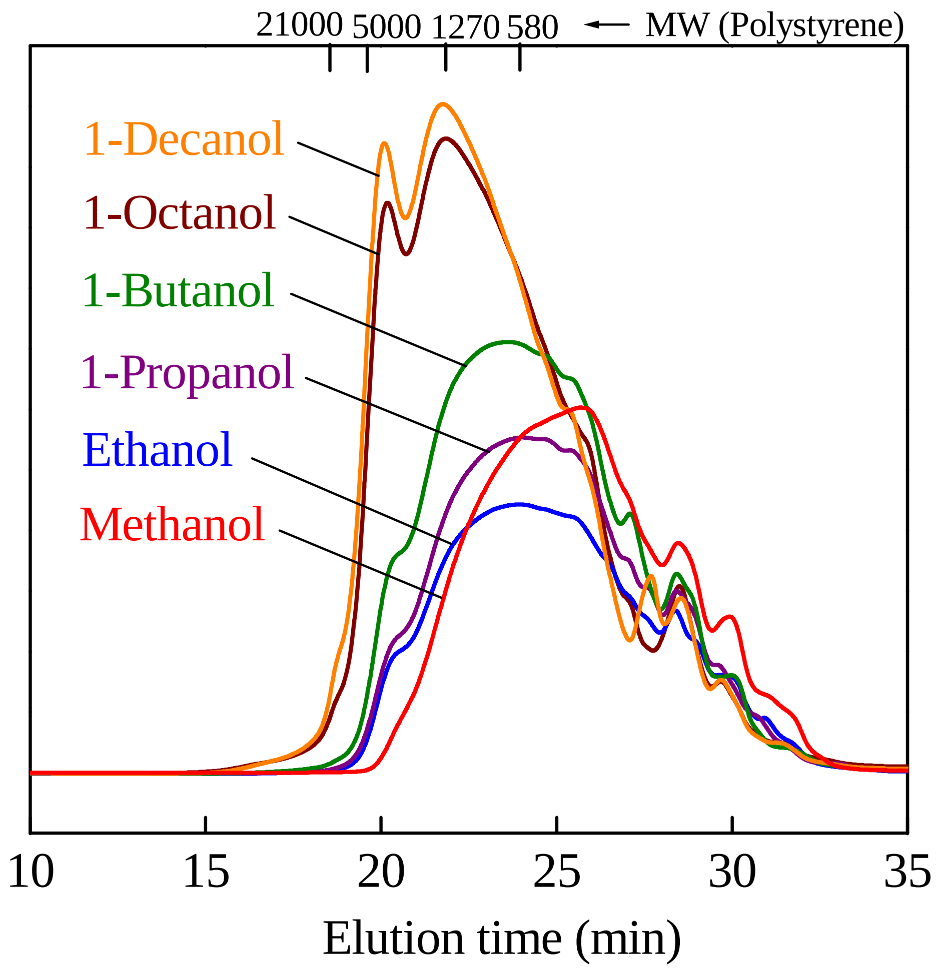
Ref: Yamazaki, Minami and Saka, 2006
J Wood Sci 52:527-532.

Various Alcohol-Soluble Portions of wood



Ref: Yamazaki, Minami and Saka, 2006
J Wood Sci 52:527-532.

Molecular Weight Distribution of Alcohol-Soluble Portions after 30 min Treatment at 350°C



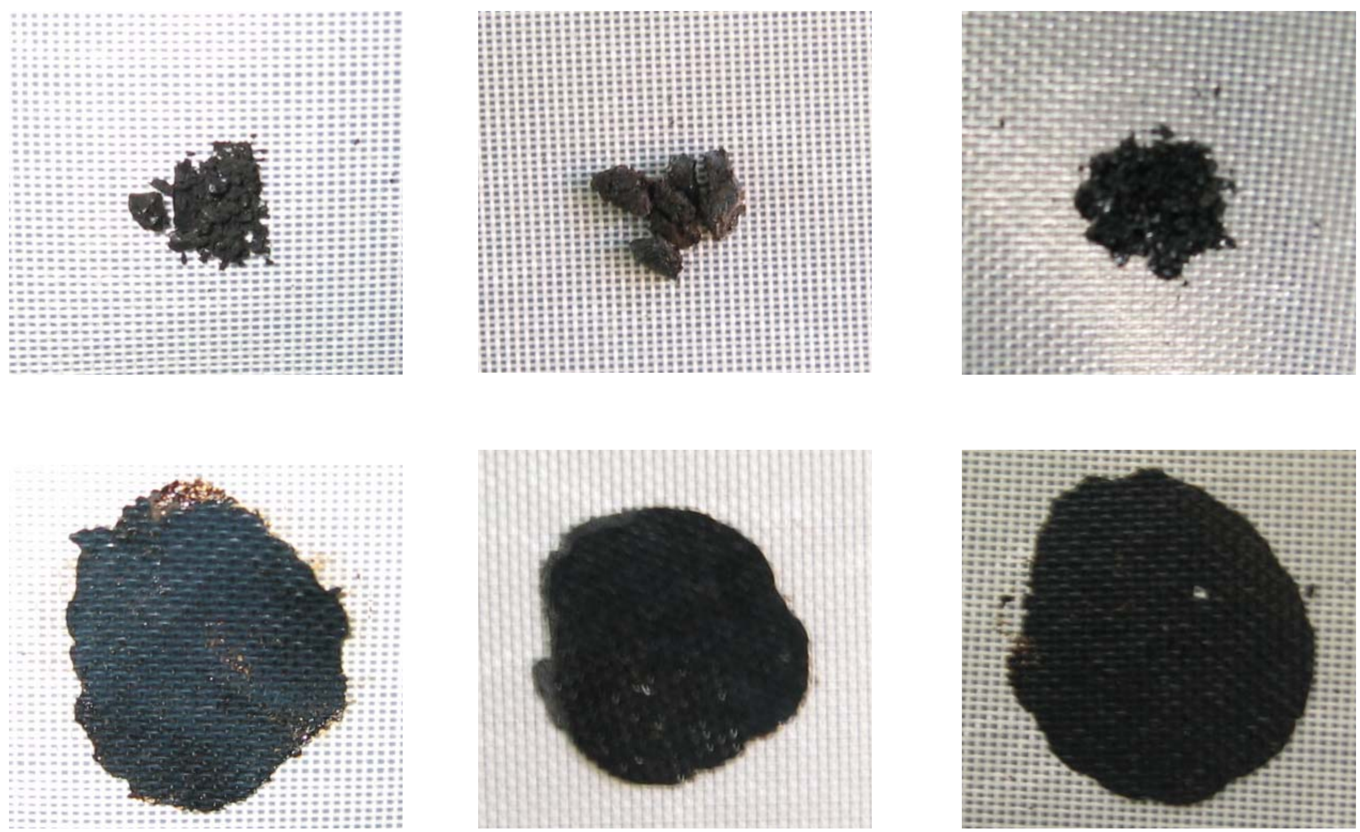
Ref: Yamazaki, Minami and Saka, 2006
J Wood Sci 52:527-532.

Octanol-Treated Sample (350 /19MPa/5Min) for Hot-Compressed Treatment at 200 for 3S

Residue | Precipitated | Mixture

Before

After



Biofuels by Supercritical Fluid Technologies

Bioplastics

Liquid Biofuel

Biochemicals

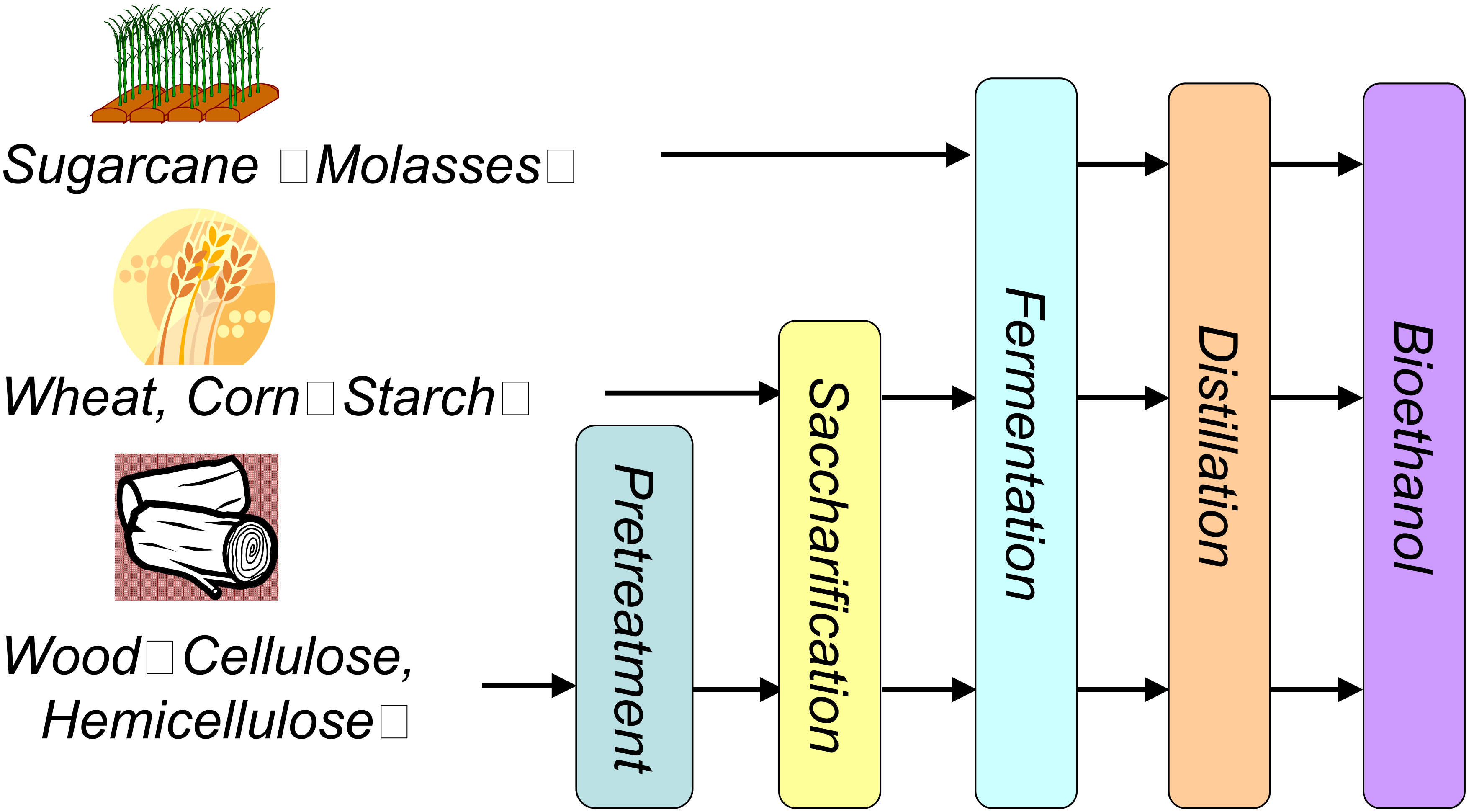
Bioethanol

Bioethanol from Lignocellulosics by Supercritical Water Technology

Organic Acids
Biomethane

Biodiesel

Various Production Types of Bioethanol



Chemical Composition of Lignocellulose

Lignocellulose□□□*Cellulose*, *Crystalline* 40□50□
Hemicelluloses, *Amorphous* 20□30□
Lignin, *Aromatic* 20□30□

.... → *Glucose* — 6C (Hexose) → *Ethanol*

....
- *Xylose*, *Arabinose*, *Rhamnose* — 5C (Pentose) → *Ethanol*

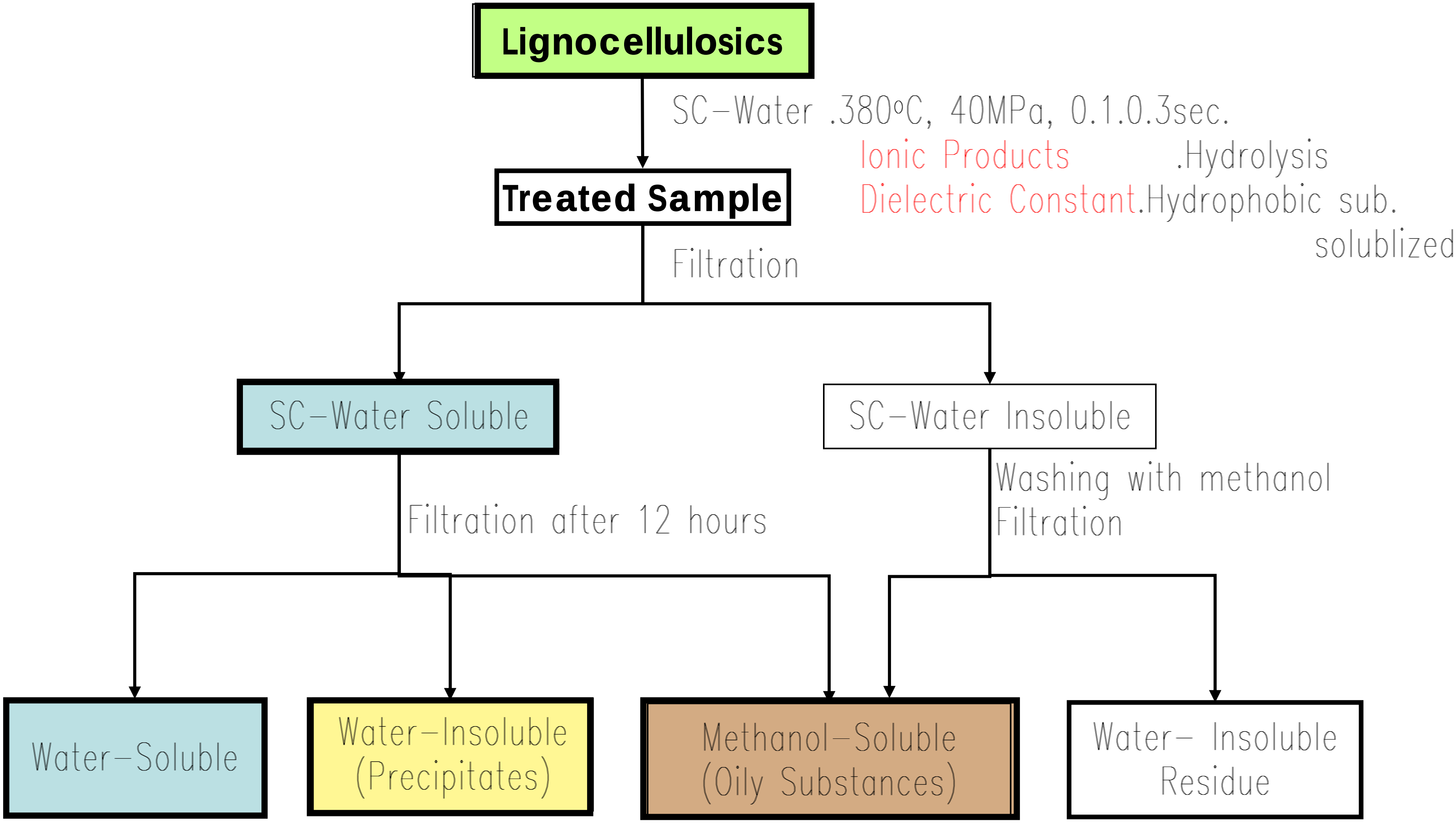
By Genetical Engineering

- ♦Bacteria□ *Zymononas mobilis*□
- ♦Colon bacteria (*Escherichia coli*)
- ♦Yeast(*Saccharomyces cerevisiae*)

- *Galactose*, *Mannose*, *Fucose*, *Glucose* — 6C (Hexose) → *Ethanol*

......

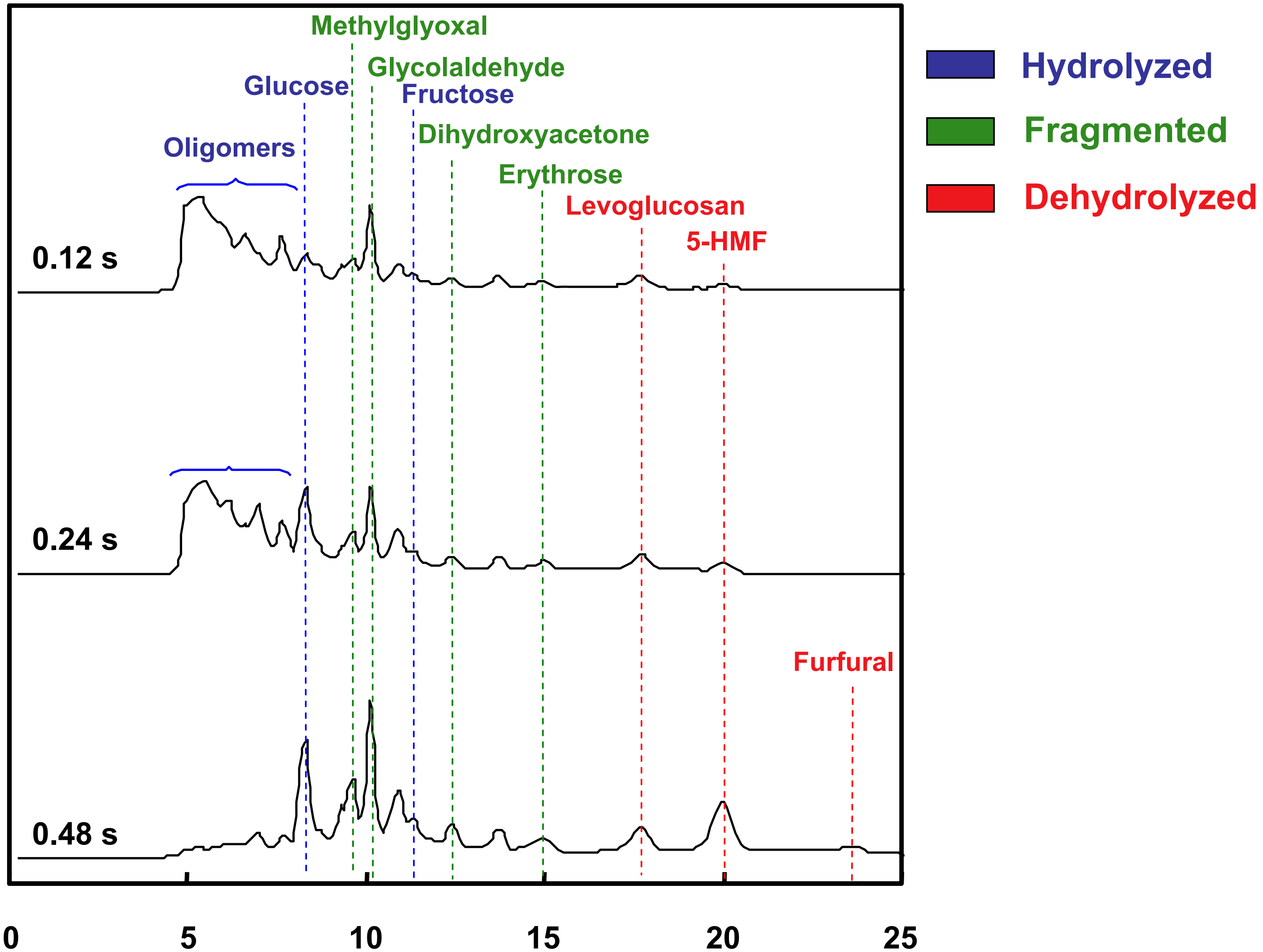
The Separation Scheme of Lignocellulosics Treated in Supercritical Water



Ref: Saka and Ehara, 2002
International Symposium on "Highly Efficient Use of Energy and Reduction of its Environmental Impact" :17-26.

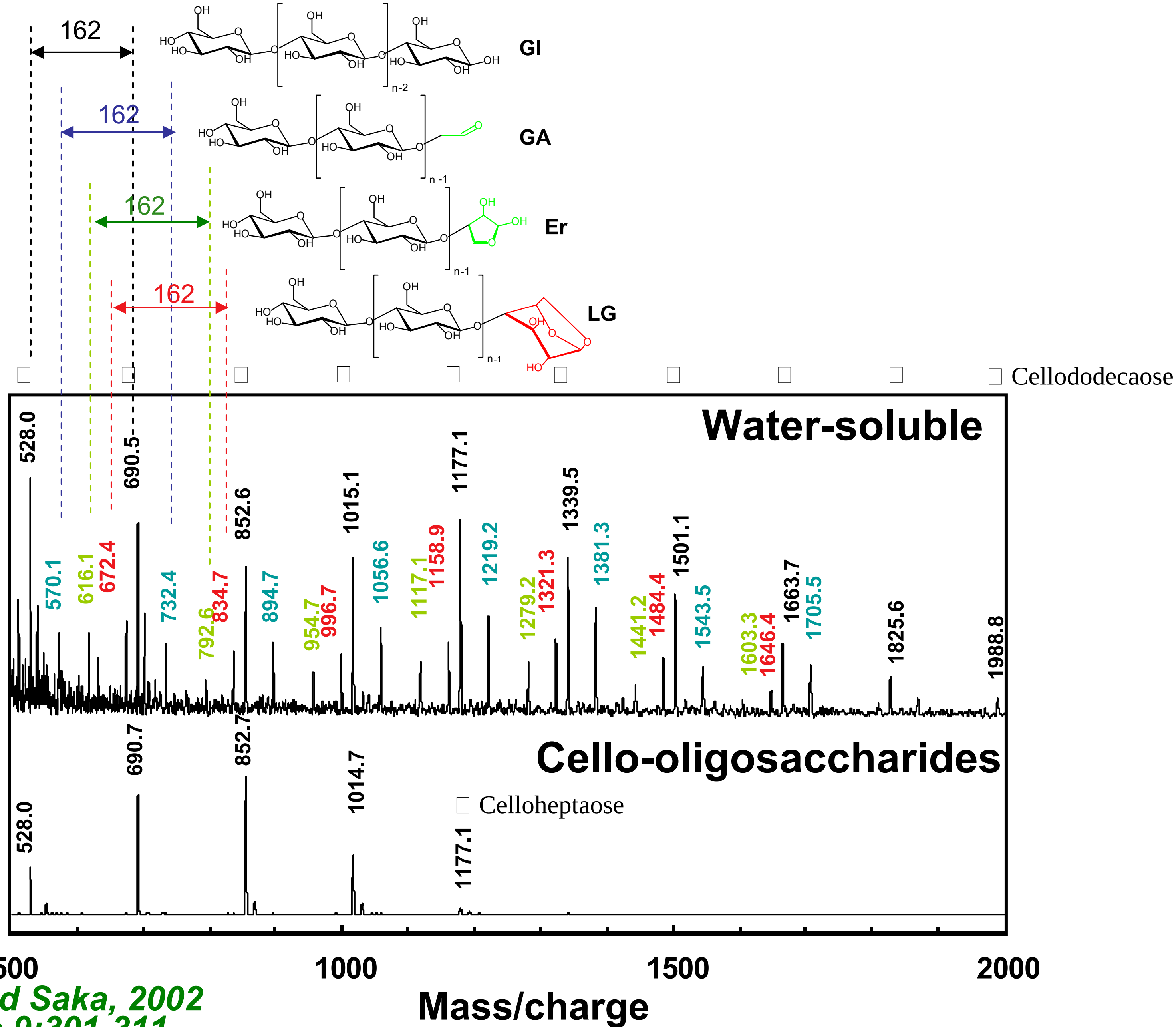
Water-Soluble Portion

HPLC Chromatograms of Water-Soluble Portions from Cellulose as Treated in Supercritical Water (380 °C, 40 MPa)



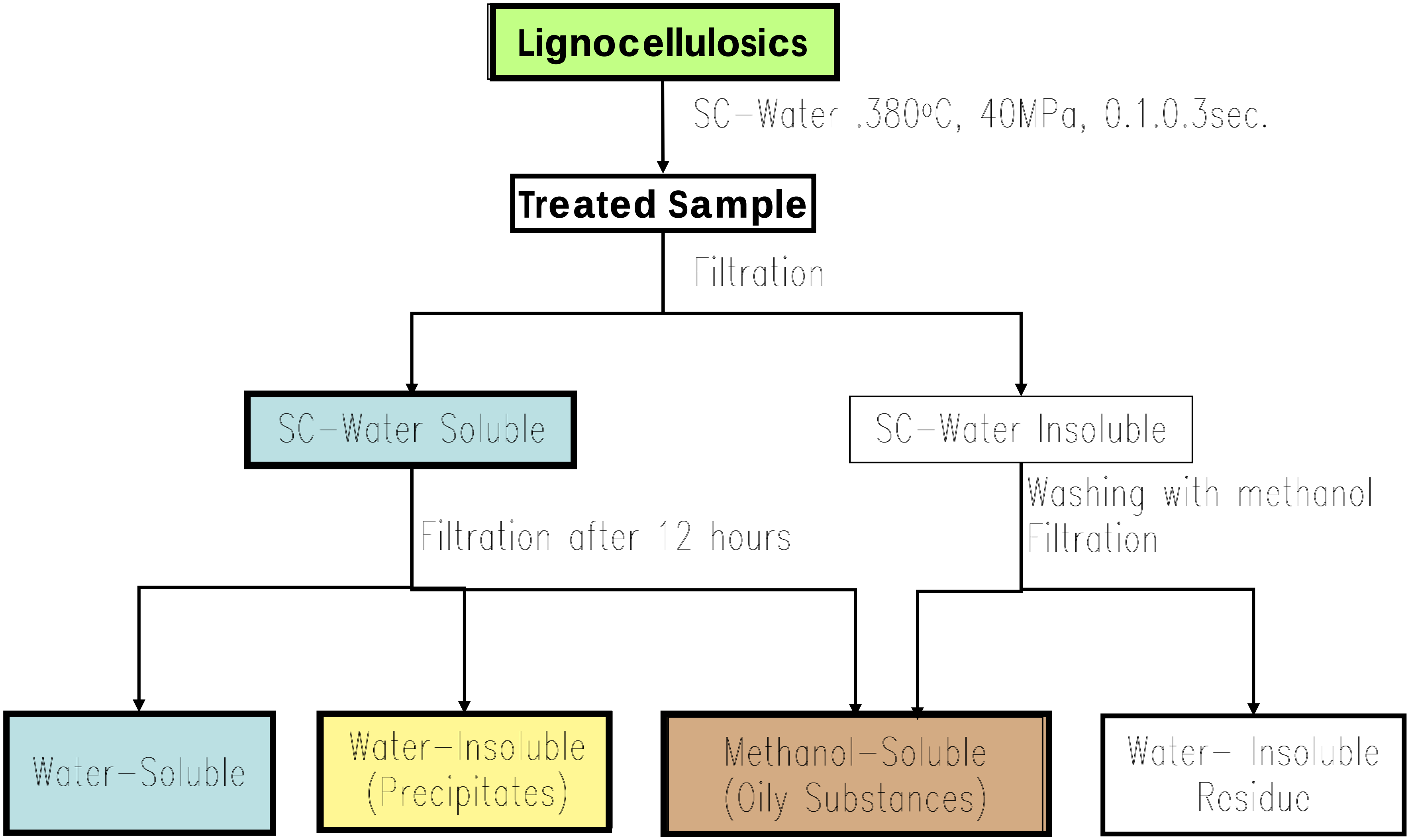
Ref: Ehara and Saka, 2002
Cellulose 9:301-311.

MALDI-TOFMS analyses of the water-soluble portion
(Flow-type system, 380 °, 40 MPa, 0.24 s)



Ref: Ehara and Saka, 2002 Cellulose 9:301-311.

The Separation Scheme of Lignocellulosics Treated in Supercritical Water



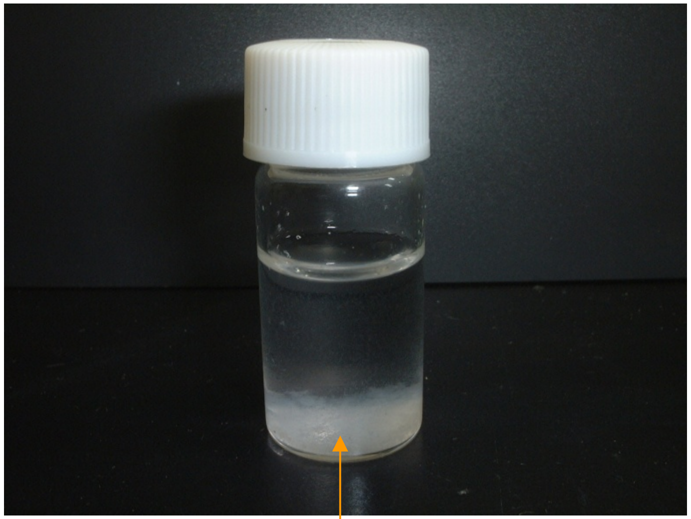
Ref: Saka and Ehara, 2002
International Symposium on "Highly Efficient Use of Energy and Reduction of its Environmental Impact" :17-26.

Precipitates from Supercritical Water-soluble Portion

SC water-soluble

After 12 h

Precipitates



SC water

Dielectric constant; 10

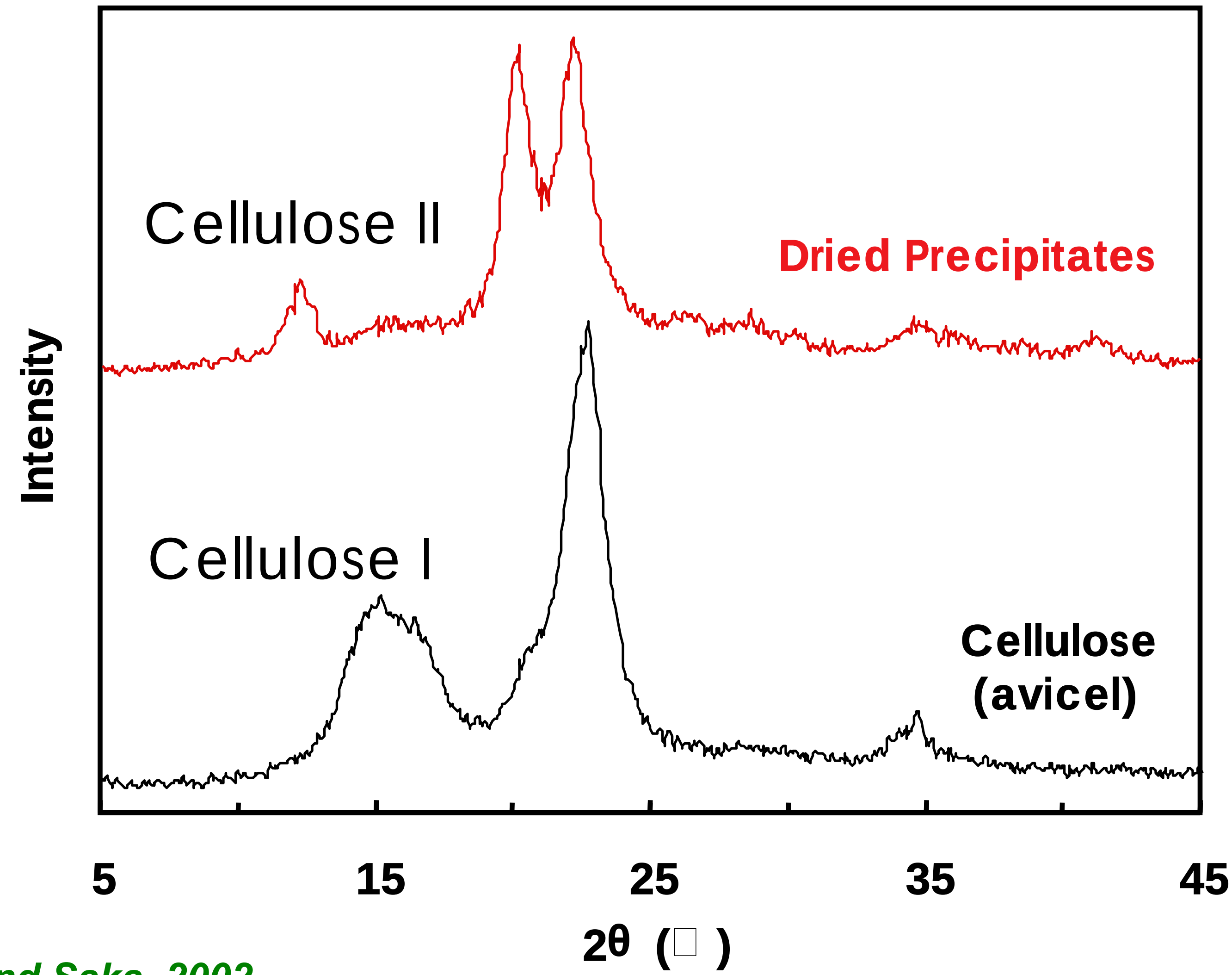
Hydrophobic

Ordinary water

Dielectric constant; 80

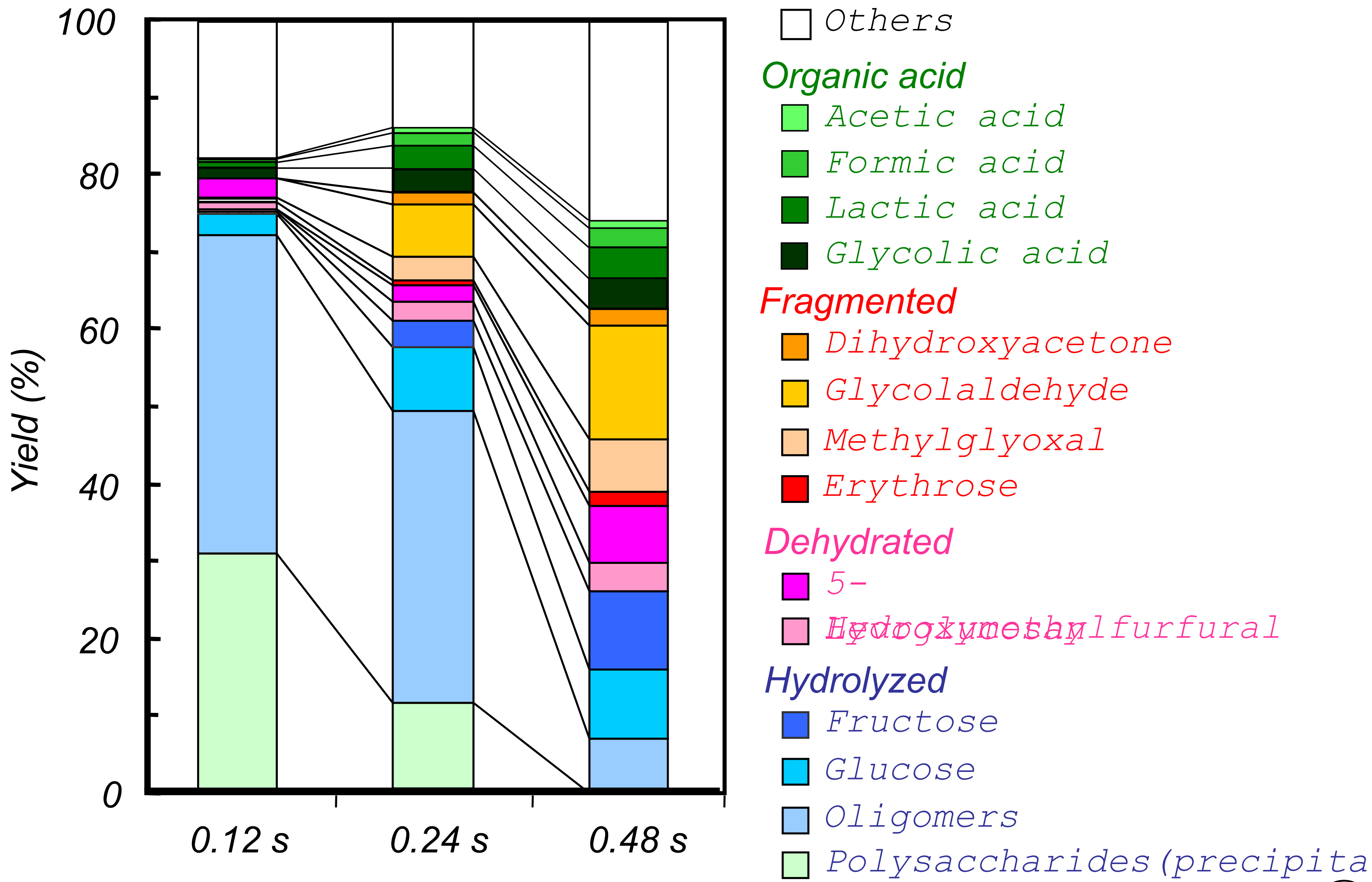
Hydrophilic

X-ray Diffractograms of Dried Precipitates after Supercritical Water Treatment at 380 °C for 0.24 s



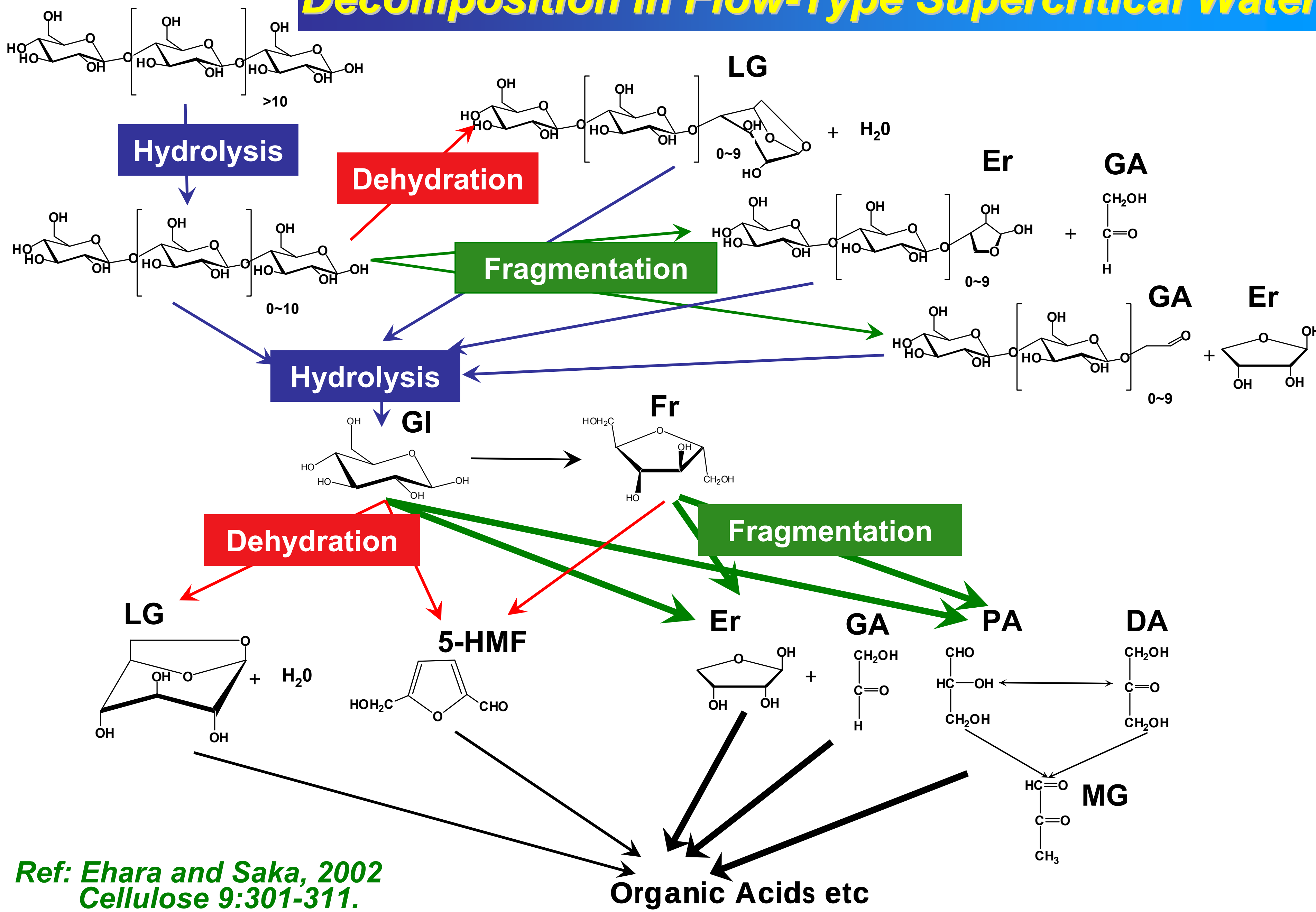
Ref: Ehara and Saka, 2002
Cellulose 9:301-311.

Chemical Composition of Cellulose Treated in Supercritical Water (380℃, 40MPa)



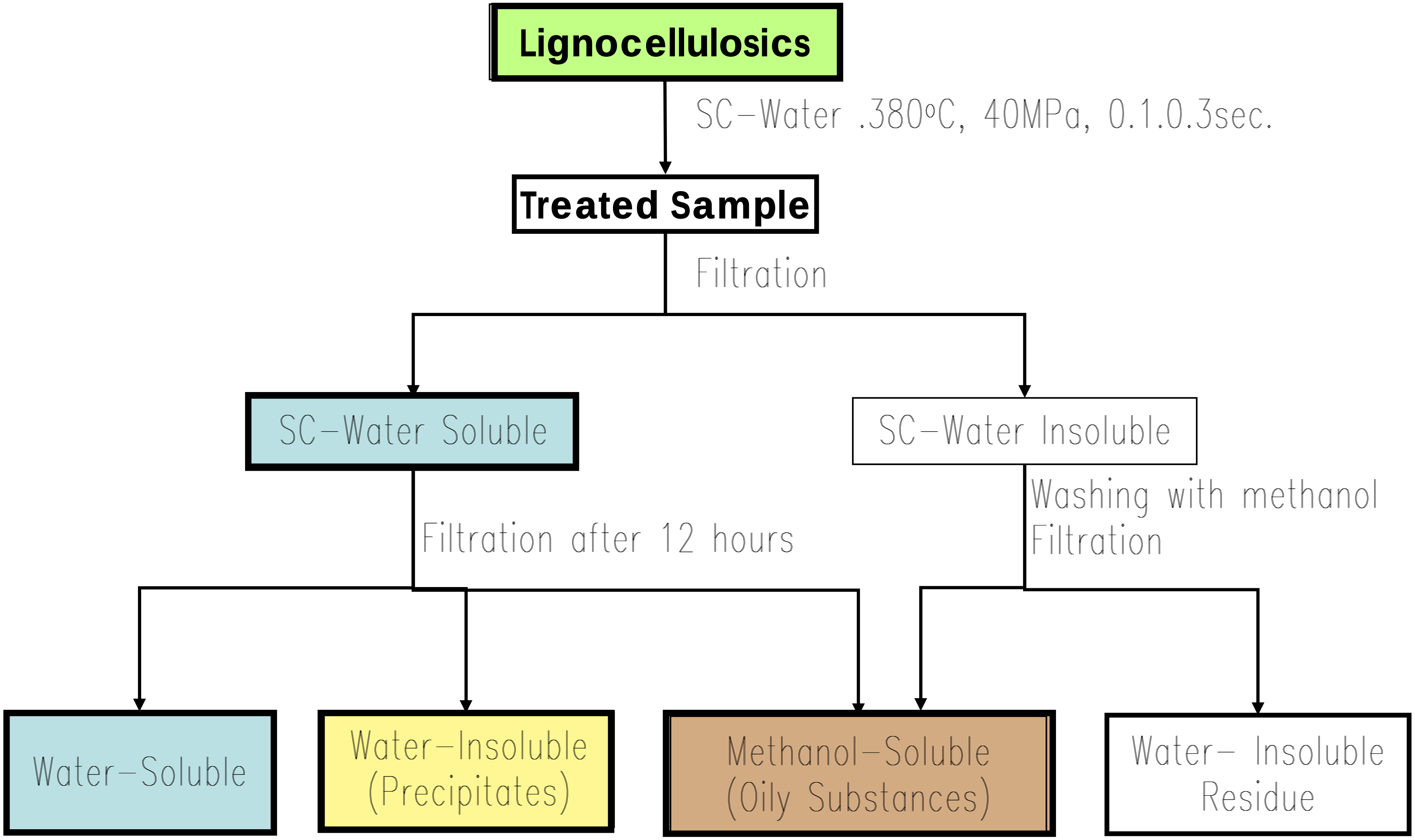
Ref: Ehara and Saka, 2002
Cellulose 9:301-311.

The Proposed Pathway of Cellulose Decomposition in Flow-Type Supercritical Water



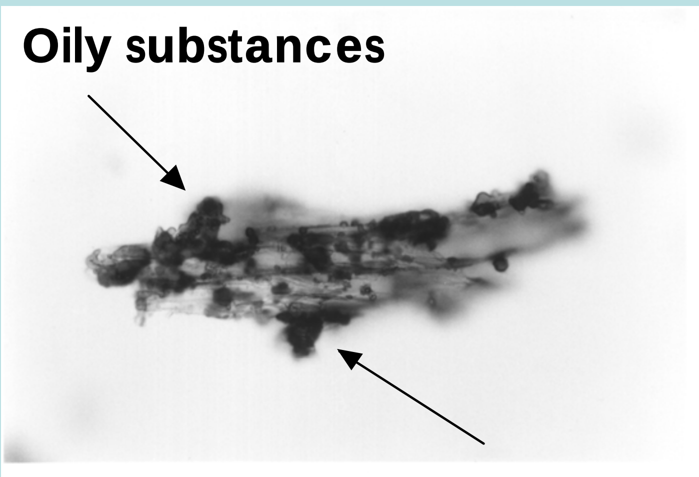
Ref: Ehara and Saka, 2002
Cellulose 9:301-311.

The Separation Scheme of Lignocellulosics Treated in Supercritical Water



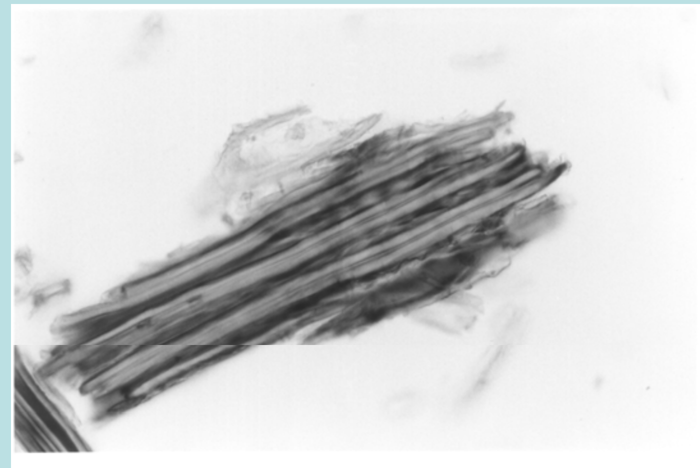
Ref: Saka and Ehara, 2002
International Symposium on "Highly Efficient Use of Energy and Reduction of its Environmental Impact" :17-26.

Oily Substances (Methanol-soluble Portion)



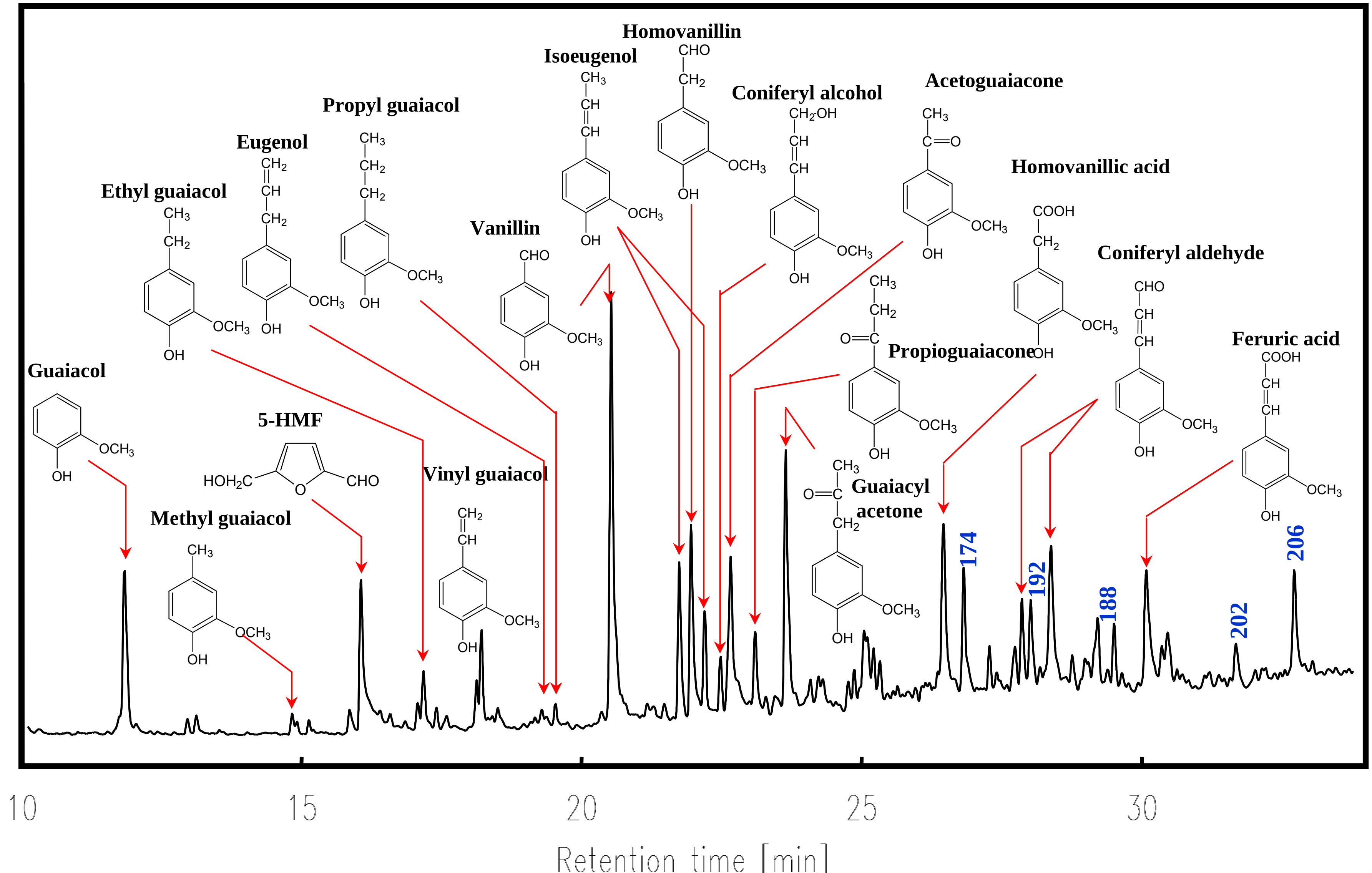
Methanol extraction

Water-insoluble residue



Methanol-soluble

GC-MS Analysis of the Monomeric Compounds in the MeOH-Soluble Portion



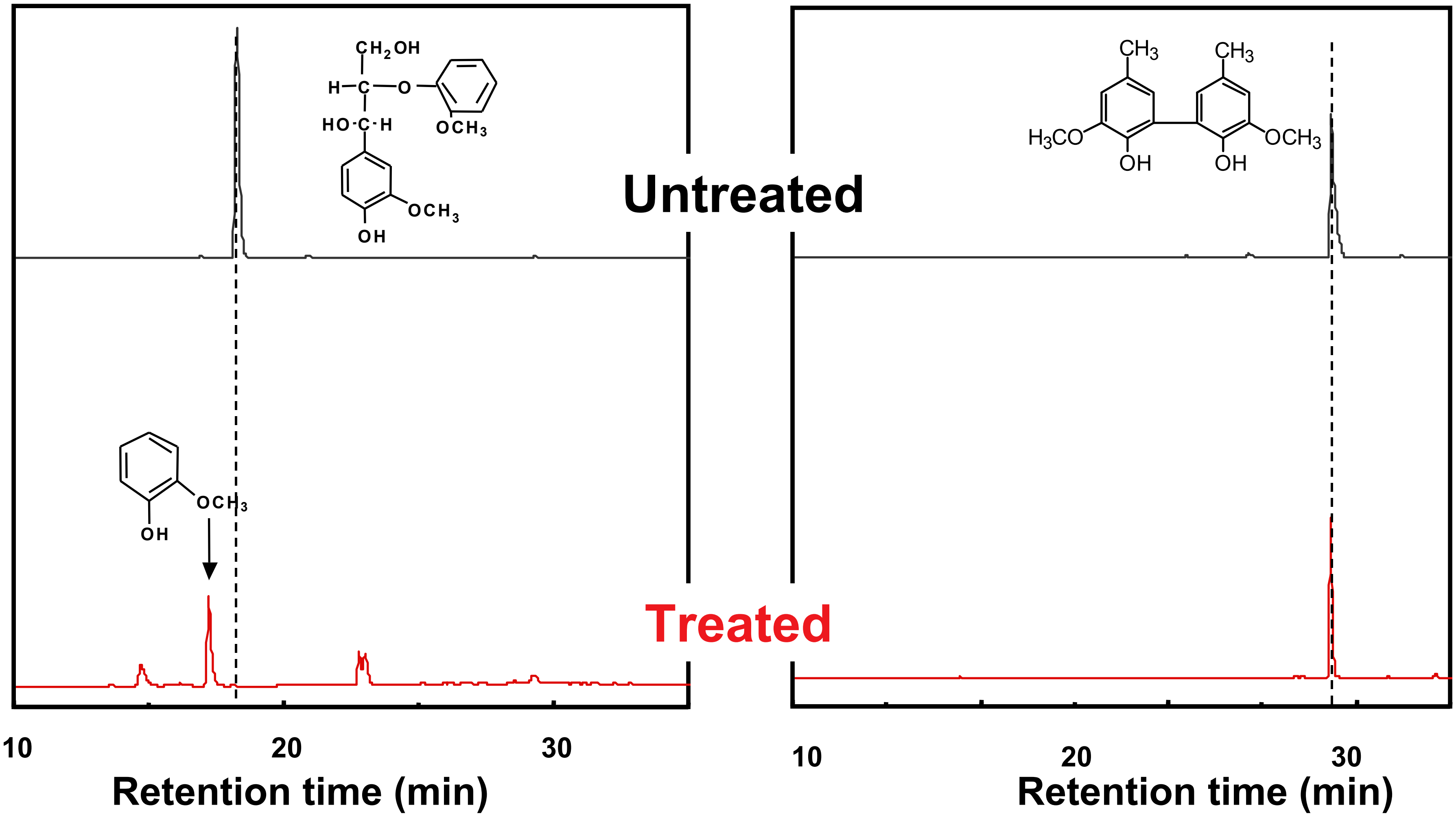
Ref: Takada, Ehara and Saka, 2004 J Wood Sci 50:253-259.

Study of Lignin Model Compounds

Supercritical water (400 °C, 115MPa)

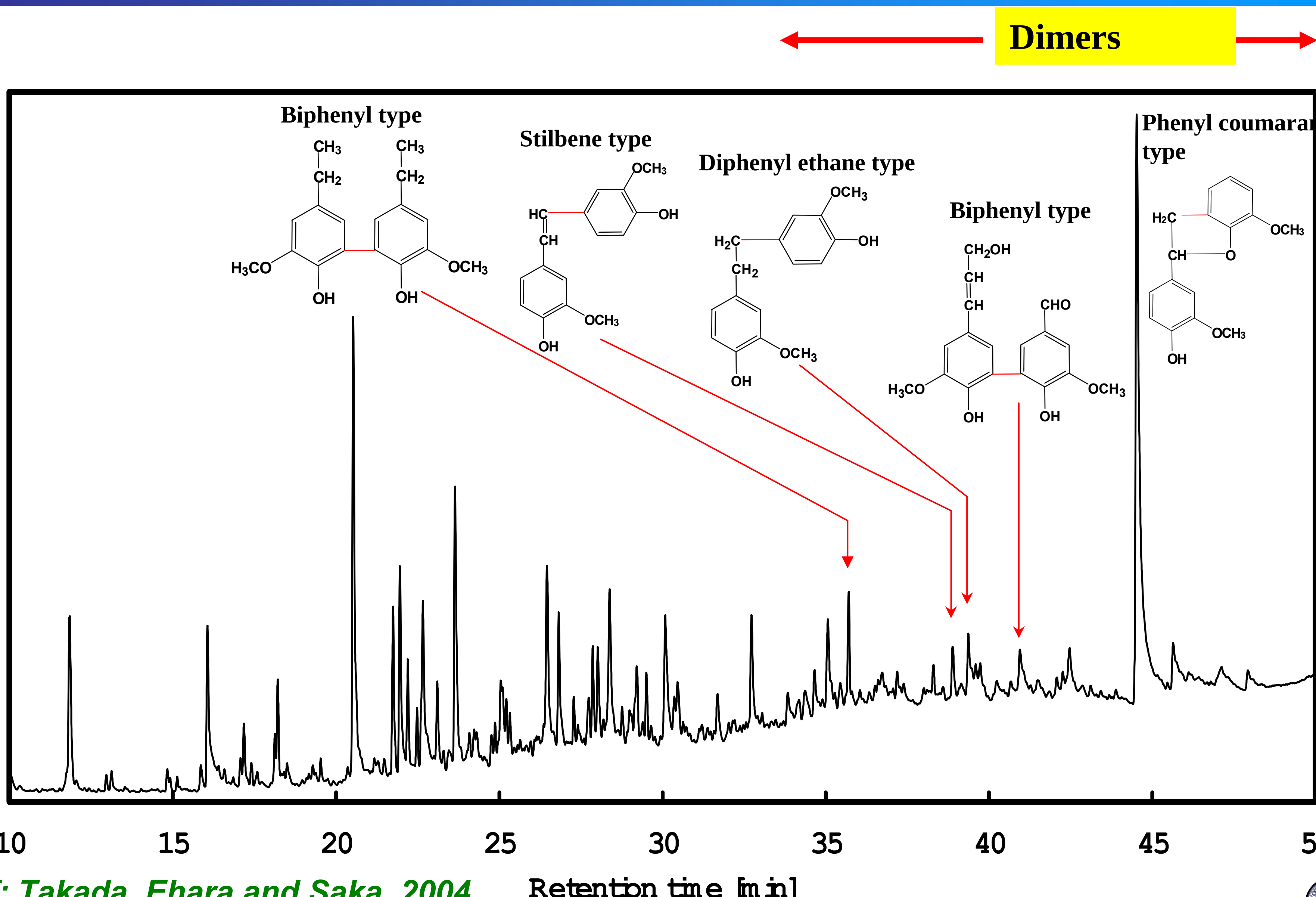
ß-O-4 Ether Linkage
Guaiacylglycerol-ß-guaiacyl ether

Biphenyl Condensed Linkage



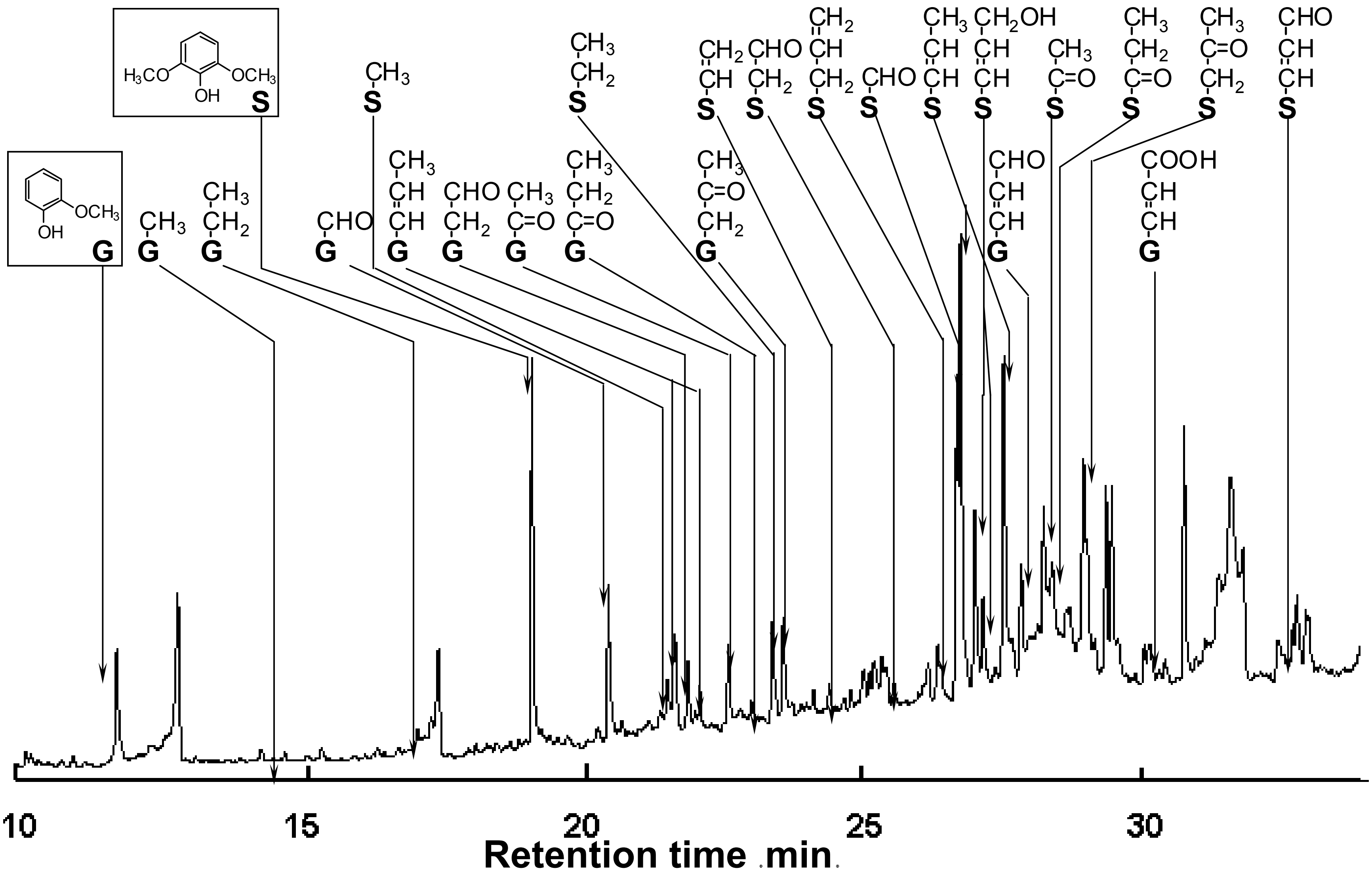
Ref: Takada, Ehara and Saka, 2004
J Wood Sci 50:253-259.

GC-MS Chromatogram of Dimeric Compounds in the MeOH-Soluble Portion



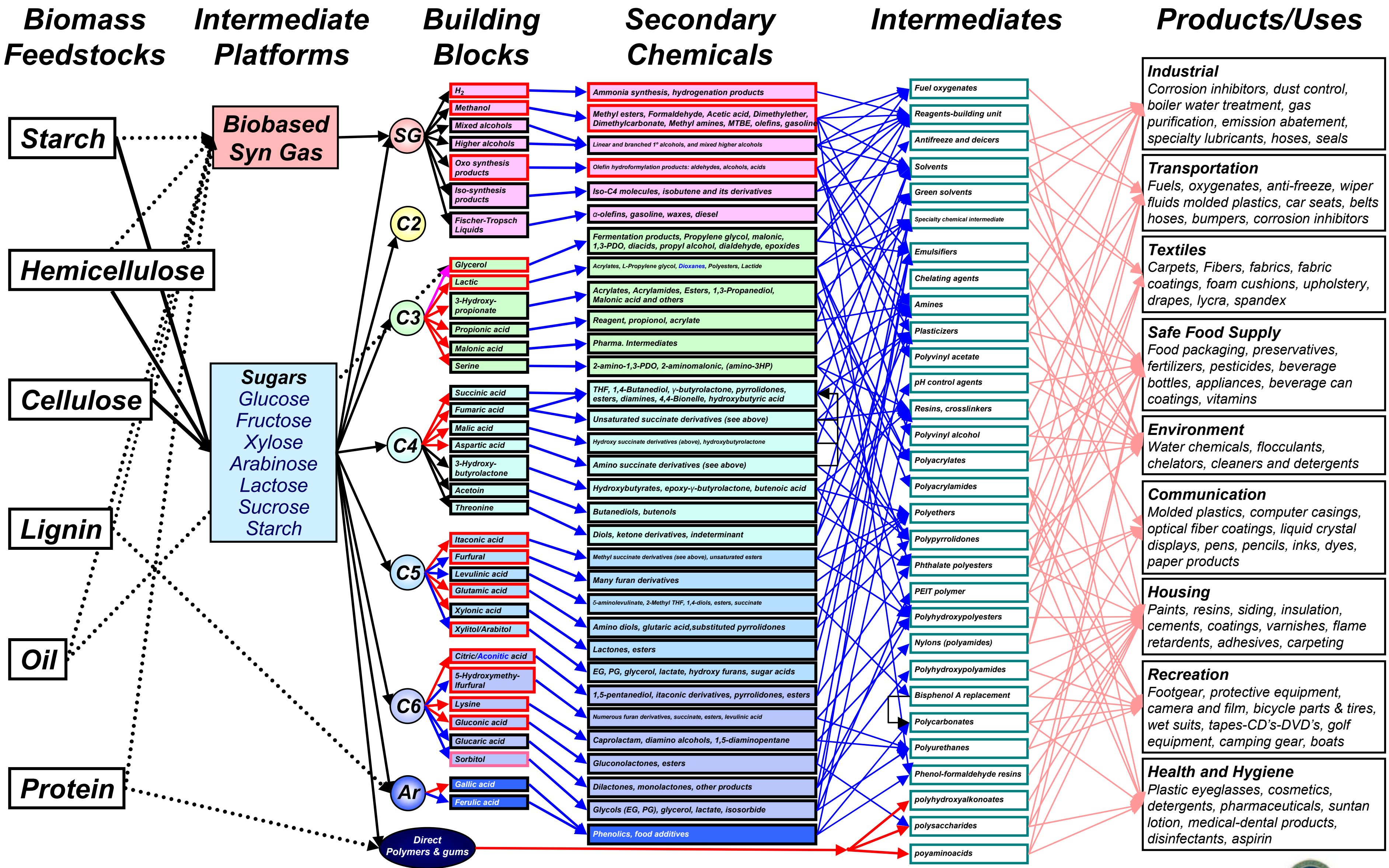
Ref: Takada, Ehara and Saka, 2004
J Wood Sci 50:253-259.

Various aromatic compounds by the GC-MS in the methanol-soluble portion from Japanese beech treated in supercritical water



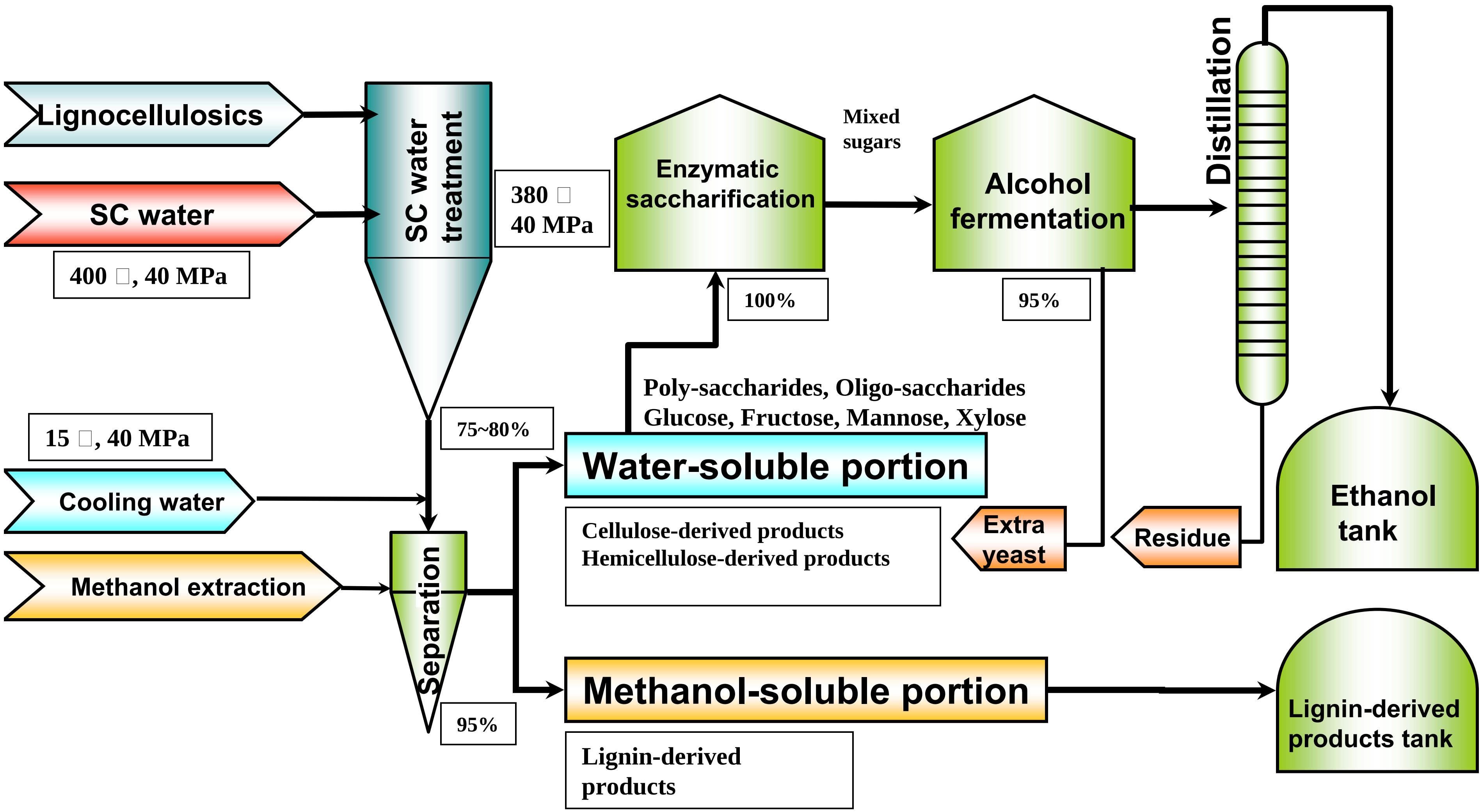
Ref: Ehara, Takada and Saka, 2005
J Wood Sci 51:256-261.

Analogous Model of a Biobased Product Flow-chart for Biomass Feedstocks



Ref: Biomass U.S. DOE, 2004, 1-76.

SC Water Process for Ethanol Production from Lignocellulosics



Ref: Saka and Ehara, 2003
Energy Res. 24:178-182.

Anaerobic Ethanol Fermentation by Yeast

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

D-Glucose   Ethanol   Carbon Dioxide

Indirect Ethanol Fermentation by Acetic Acid Fermentation

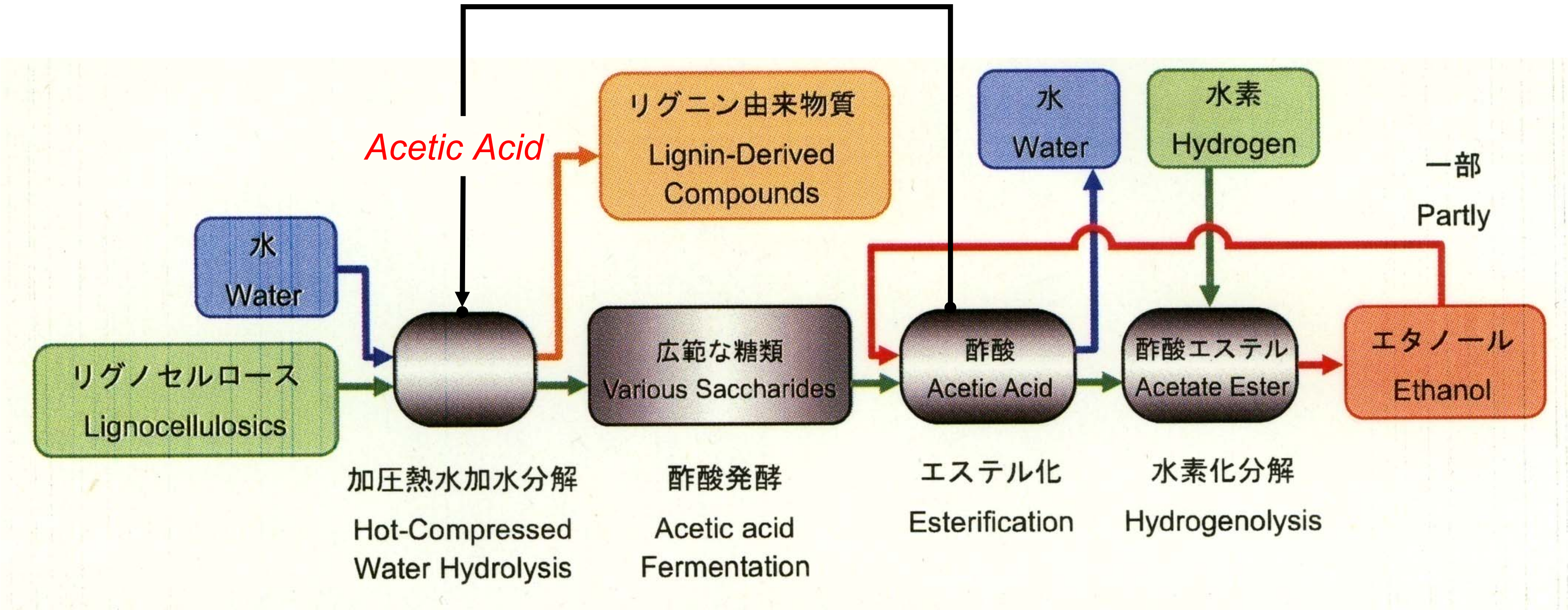
$$C_6H_{12}O_6 + H_2 \rightarrow 3\ CH_3CH_2OH + H_2O$$

D-Glucose Hydrogen   Ethanol   water

AcOH Fermentation→ Esterification→ Hydrogenolysis

NEDO Development of Preparatory Basic Bioenergy Technologies

Ethanol Production by Acetic Acid Fermenation with Hydrogenolysis from Lignocellulosics



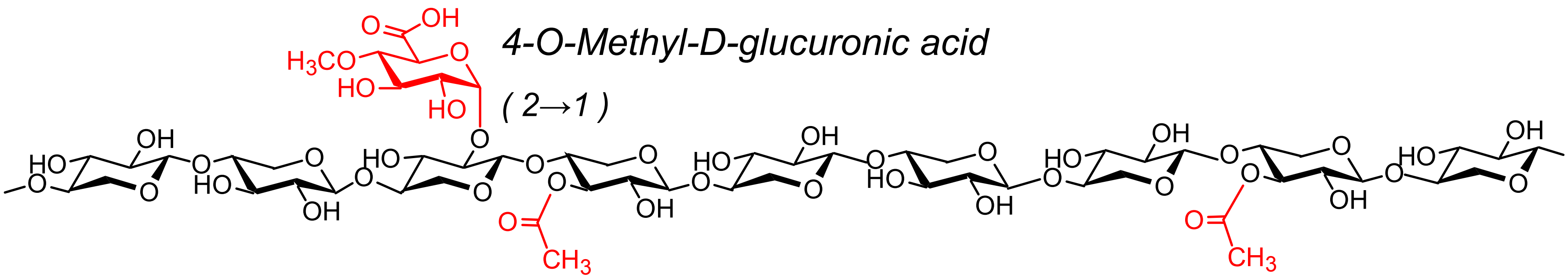
Hot-Compressed Water Hydrolysis | *Acetic Acid Fermentation* | *Esterification/ Hydrogenolysis*

Ref: NEDO Pamphlet, p.20 (Oct 12,2007)

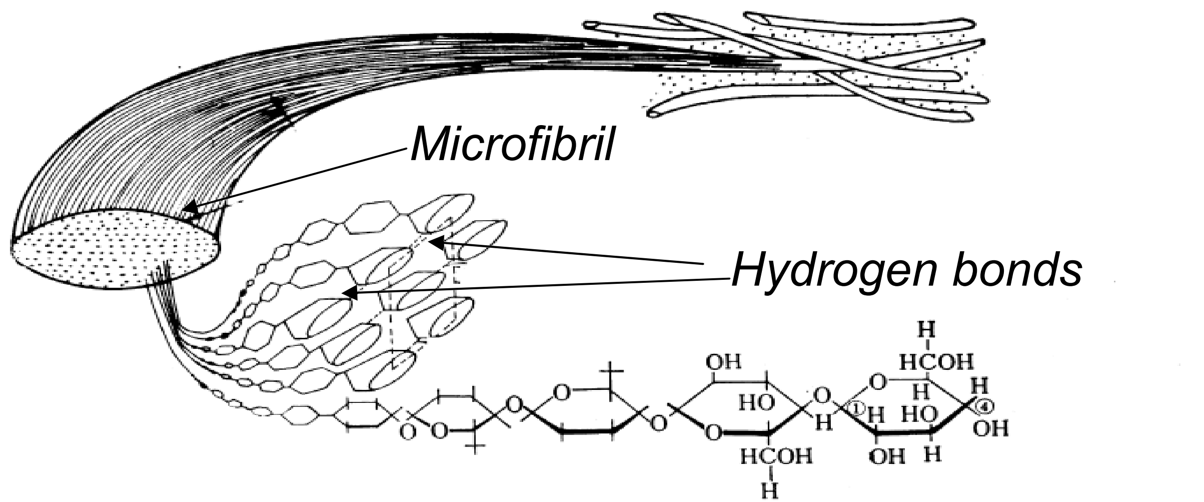
Hardwood Xylan (Hemicellulose) and Cellulose

Hardwood Xylan □ 90%□

O-Acetyl-4-O-methylglucuronoxylan

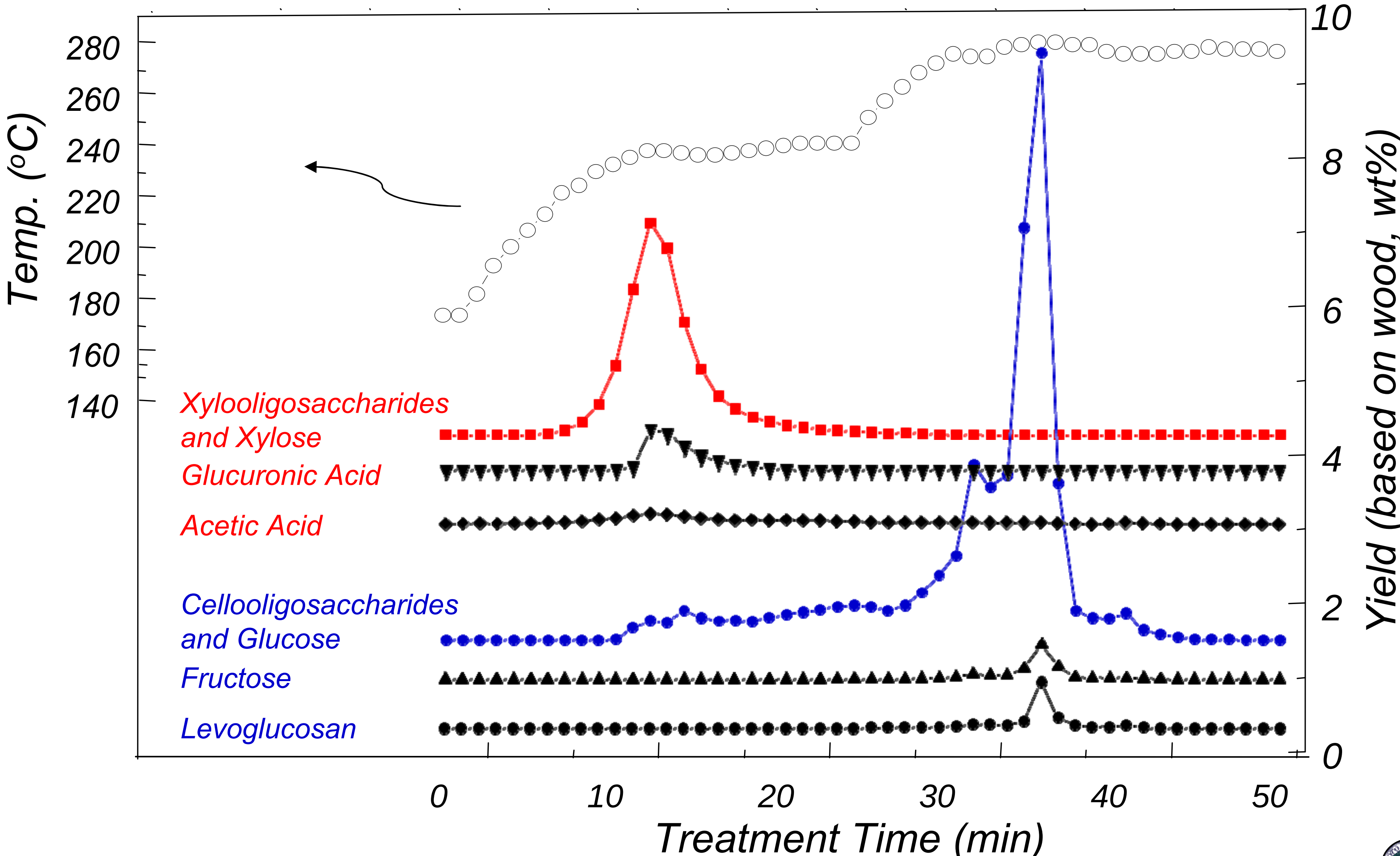


Cellulose

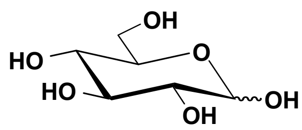


Ref: Wood Chemistry, Kyoritsu Publisher,1968.

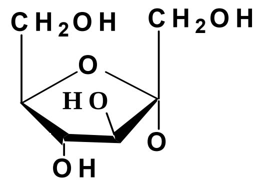
Buna Wood Hydrolysis as Treated by Two-Step Hot-Compressed (230-270/10MPa/10mL/min)



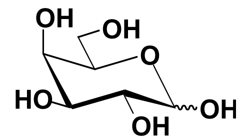
Substrates for Acetic Acid Fermentation



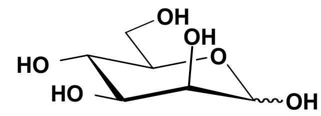
D-Glucose
(C6)



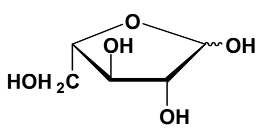
D-Fructose
(C6)



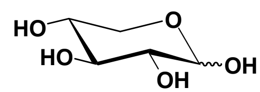
D-Galactose
(C6)



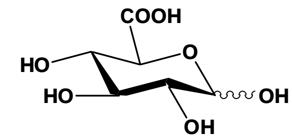
D-Mannose
(C6)



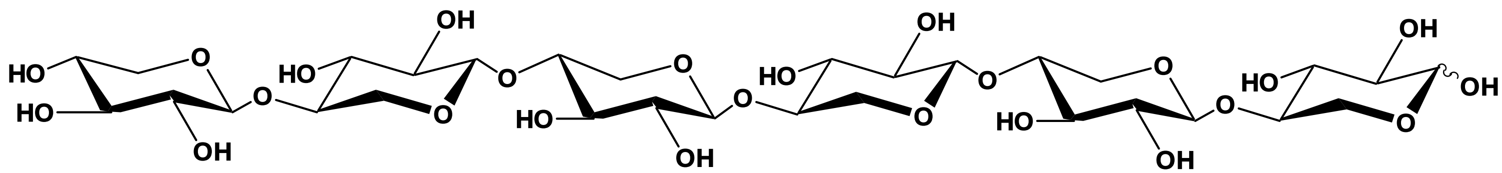
L-Arabinose
(C5)



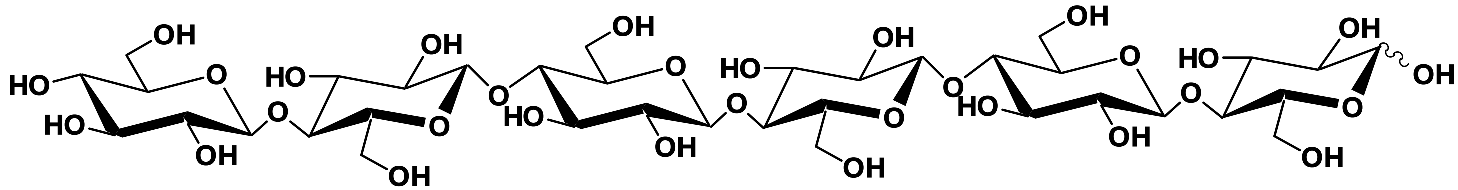
D-Xylose
(C5)



Uronic acids
(Acid Sugar)



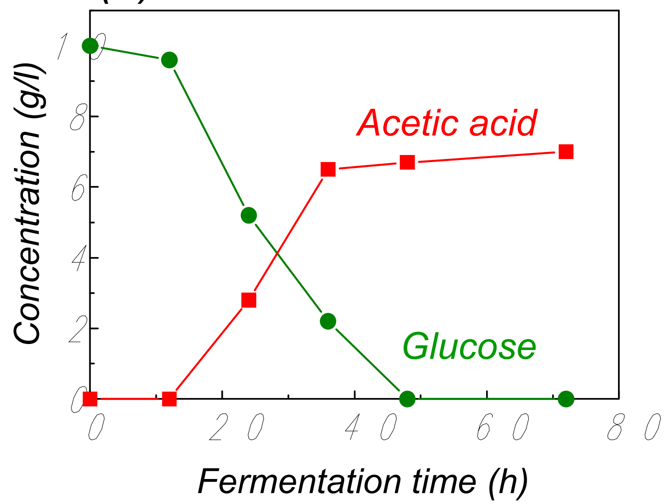
Xylooligosaccharide



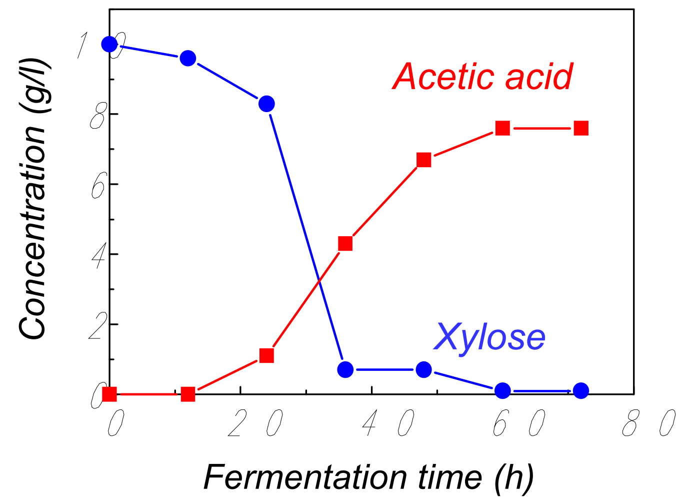
Cellooligosaccharide

Acetic Acid Fermentation for sugars
– Clostridium thermoaceticum –

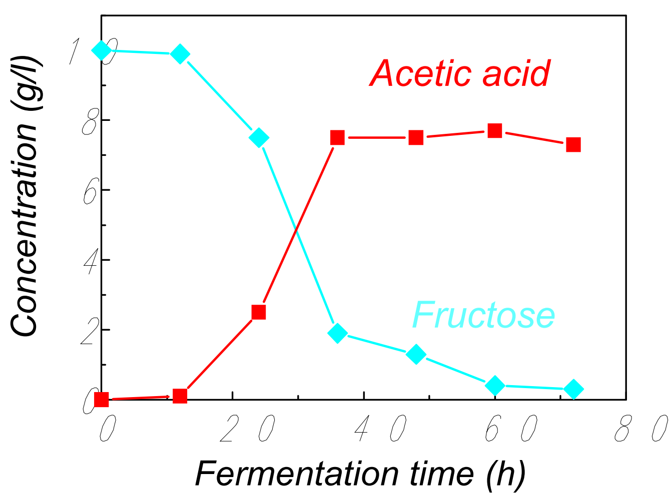
(a) Glucose



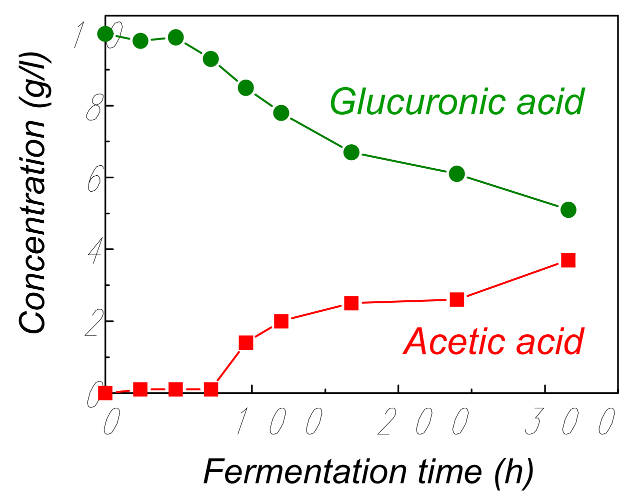
(b) Xylose



(c) Fructose

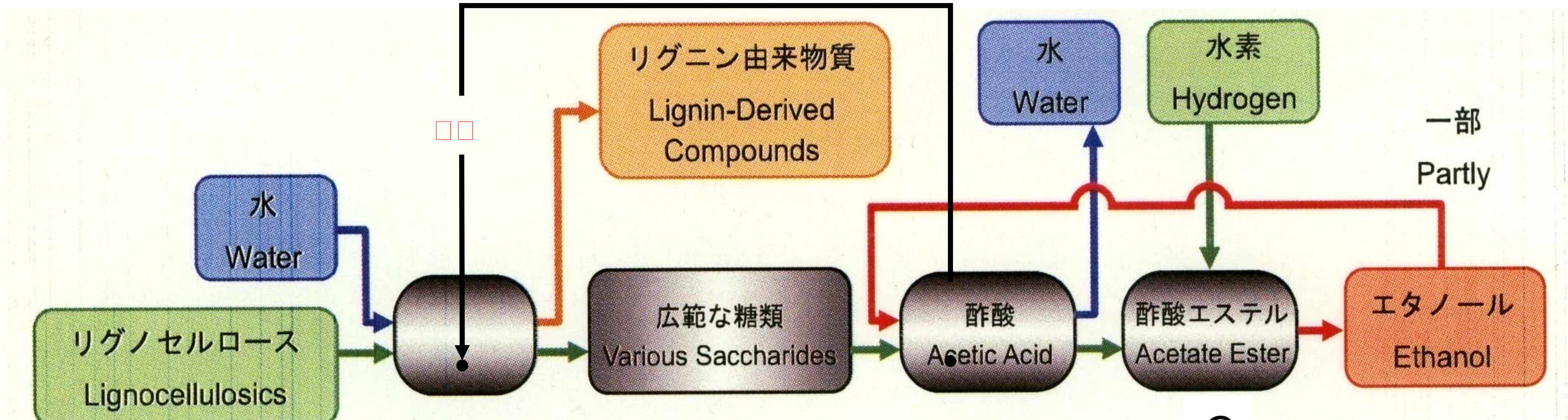


(d) Glucuronic acid



NEDO Development of Preparatory Basic Bioenergy Technologies

Ethanol Production by Acetic Acid Fermenation with Hydrogenolysis from Lignocellulosics



Fermentation $$C_6H_{12}O_6 \longrightarrow 3\ CH_3\overset{O}{C}OH$$

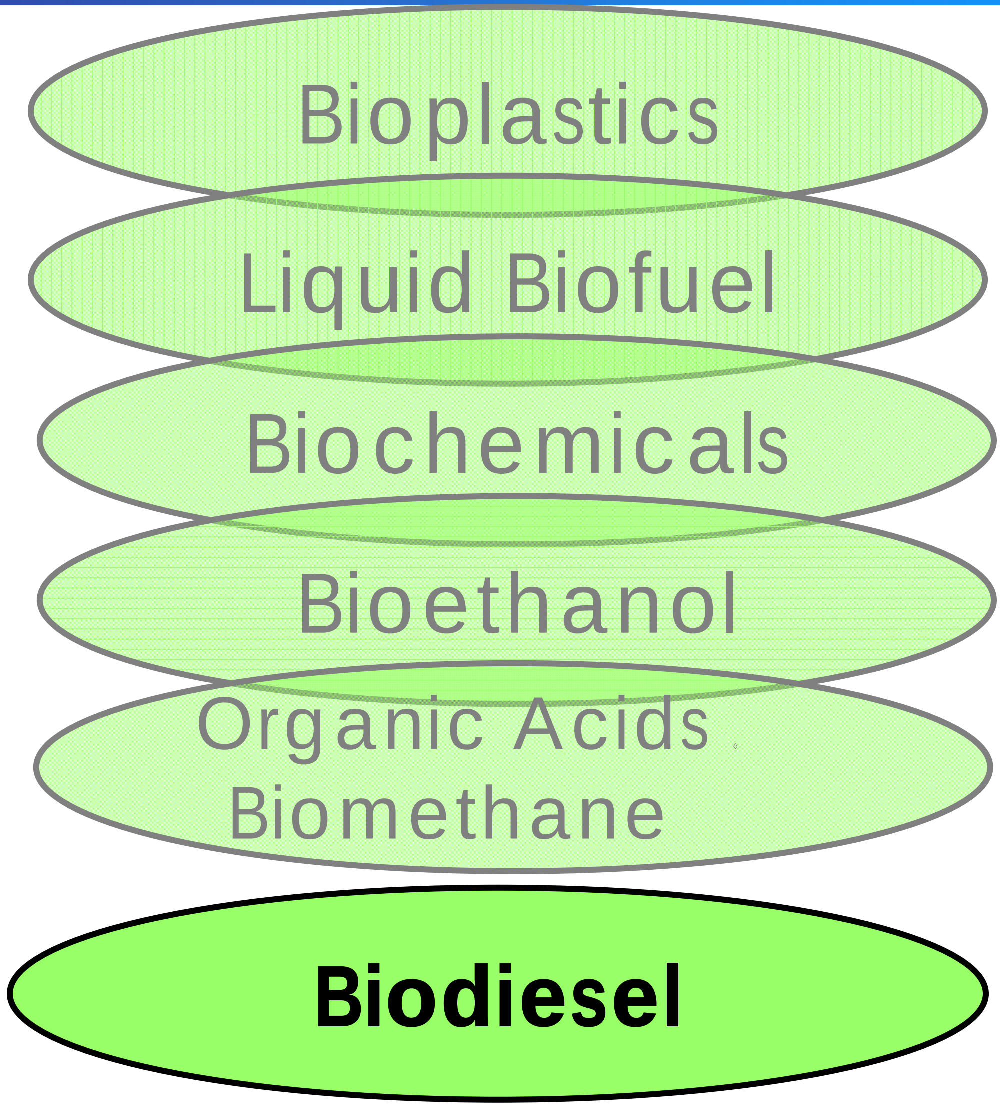
Esterification $$3\ CH_3\overset{O}{C}OH + 3\ ROH \longrightarrow 3\ CH_3\overset{O}{C}OR + 3\ H_2O$$

Hydrogenolysis $$3\ CH_3\overset{O}{C}OR + 6\ H_2 \longrightarrow 3\ CH_3CH_2OH + 3\ ROH$$

Net $$C_6H_{12}O_6 + 6\ H_2 \longrightarrow 3\ CH_3CH_2OH + 3\ H_2O$$

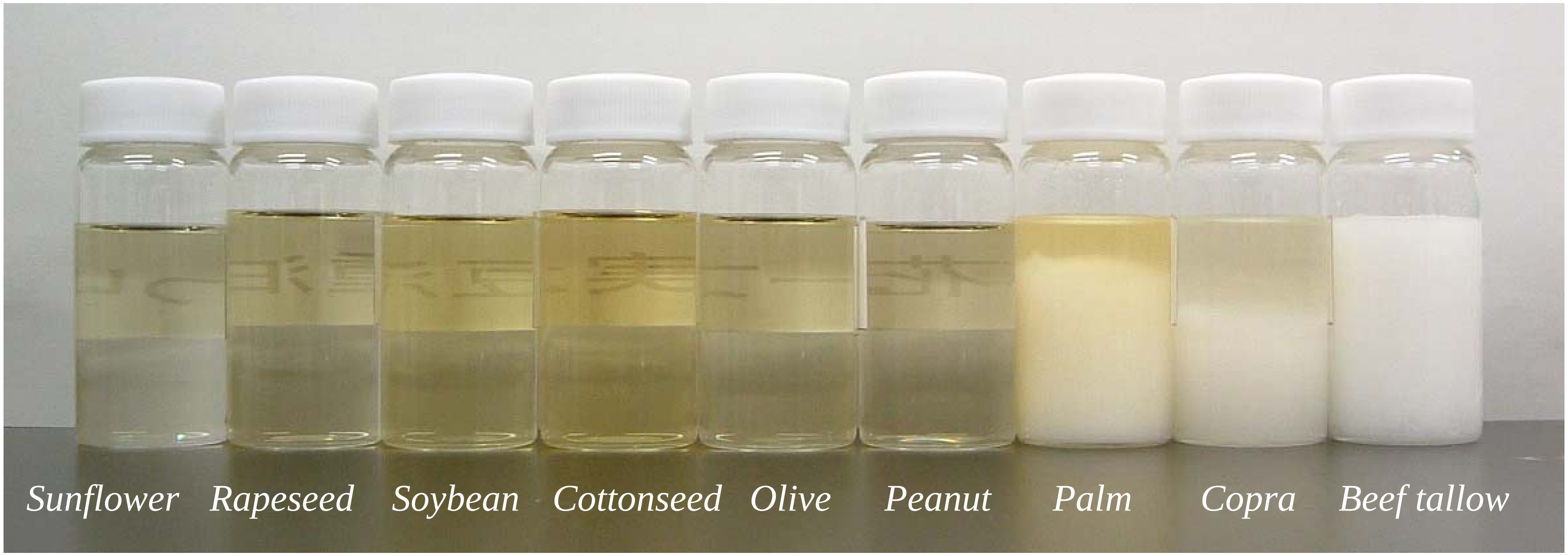
Ref: NEDO Pamphlet, p.20 (Oct 12,2007)

Biofuels by Supercritical Fluid Technologies



Biodiesel from Oils/Fats by Supercritical Methanol Technology

A Variety of Vegetable Oils and Animal Fats



Oils/Fats as Feedstocks for Biodiesel

◆Triglyceride → major component

$$\begin{array}{l} CH_2-OCOCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \\ | \\ CH-OCOCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \\ | \\ CH_2-OCOCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \end{array}$$

Triolein

◆Free fatty acid → minor component (2-5%)
Waste oil 25%

$$HOOCCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

Oleic acid

Alkali-catalyzed Method for Commercial Biodiesel Production

◆Transesterification

$$
\begin{array}{l} CH_2-OCOR^1 \\ | \\ CH-OCOR^2 \\ | \\ CH_2-OCOR^3 \end{array}
\quad + \quad 3CH_3OH \quad \xrightarrow{\text{Alkaline catalyst}} \quad
\begin{array}{l} R^1COOCH_3 \\ \\ R^2COOCH_3 \\ \\ R^3COOCH_3 \end{array}
\quad + \quad
\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}
$$

Triglyceride — Biodiesel

◆Saponification

$$
R^4COOH \quad + \quad KOH \quad \xrightarrow{\text{Alkaline catalyst}} \quad R^4COOK \quad + \quad H_2O
$$

Free fatty acid — Alkaline catalyst — Saponified product

Catalyst-free
Supercritical Methanol (SC MeOH) Methods

◆**One-Step SC MeOH Method :**

(Saka Method)

Transesterification

Ref: Saka and Kusdiana, 2001, Fuel 80:225-231.

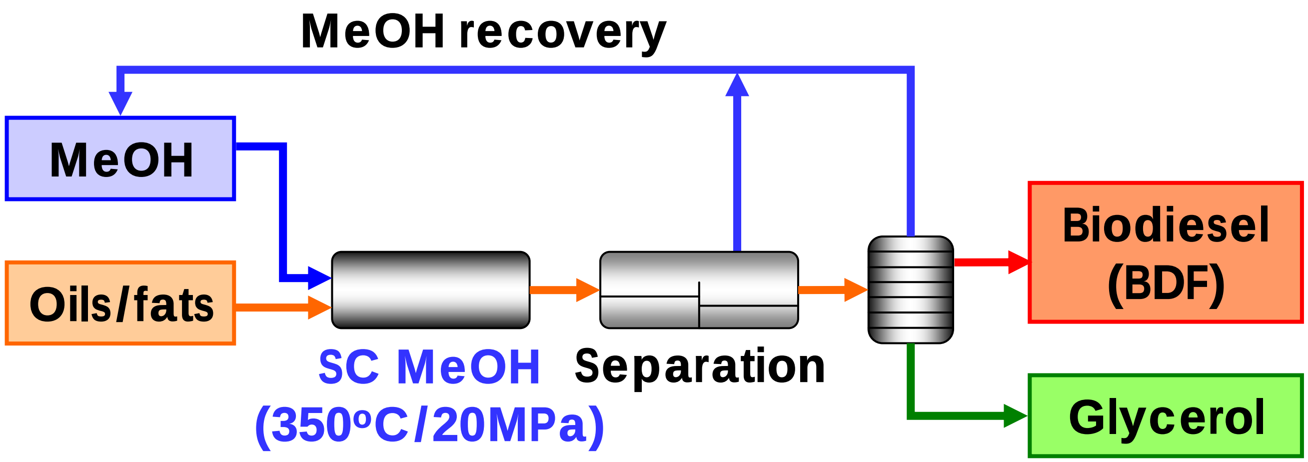
◆**Two-Step SC MeOH Method :**

(Saka-Dadan Method)

Hydrolysis + Esterification

Ref: Kusdiana and Saka, 2004, Appl Biochem Biotech 115:781-791.

One-Step SC MeOH Method (Saka Process)



Transesterification

$$\begin{matrix} CH_2\text{–}OCOR^1 \\ | \\ CH\text{–}OCOR^2 \\ | \\ CH_2\text{–}OCOR^3 \end{matrix} + 3CH_3OH \xrightarrow{\text{No catalyst}} \begin{matrix} R^1COOCH_3 \\ R^2COOCH_3 \\ R^3COOCH_3 \end{matrix} + \begin{matrix} CH_2\text{–}OH \\ | \\ CH\text{–}OH \\ | \\ CH_2\text{–}OH \end{matrix}$$

Triglyceride → *Biodiesel*

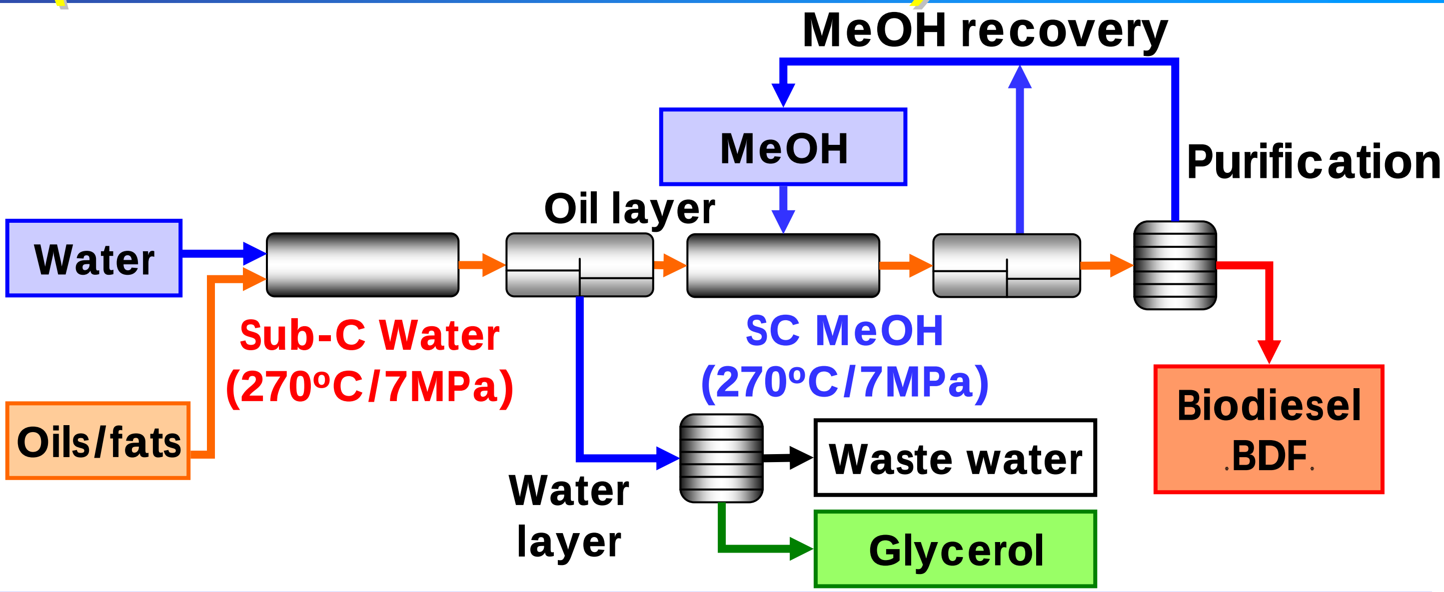
Esterification

$$R^4COOH + CH_3OH \xrightarrow{\text{No catalyst}} R^4COOCH_3 + H_2O$$

Free fatty acid → *Biodiesel*

Ref: Saka and Kusdiana, 2001, Fuel 80:225-231.

Two-Step SCMeOH Method (Saka-Dadan Process)



Step I: Hydrolysis

$$\begin{array}{l} CH_2 - OCOR^1 \\ | \\ CH - OCOR^2 \\ | \\ CH_2 - OCOR^3 \end{array} + 3H_2O \Rightarrow \begin{array}{l} R^1COOH \\ R^2COOH \\ R^3COOH \end{array} + \begin{array}{l} CH_2 - OH \\ | \\ CH - OH \\ | \\ CH_2 - OH \end{array}$$

Triglyceride — *Fatty acids*

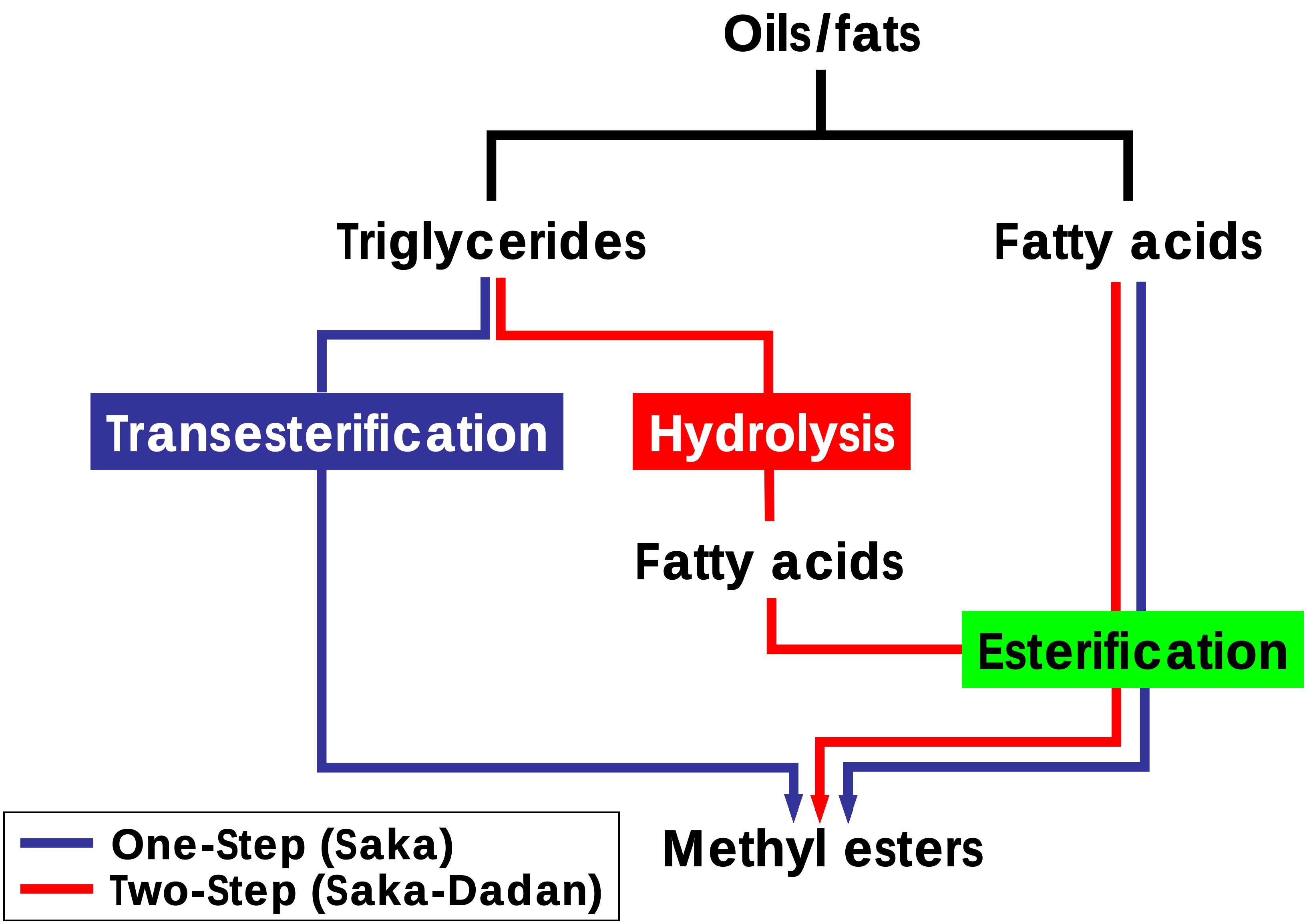
Step II: Esterification

$$R^4COOH + CH_3OH \Rightarrow R^4COOCH_3 + H_2O$$

Fatty acid — *Biodiesel*

Ref: Kusdiana and Saka, 2004, Appl Biochem Biotech 115:781-791.

Reactions Involved in SC MeOH Methods

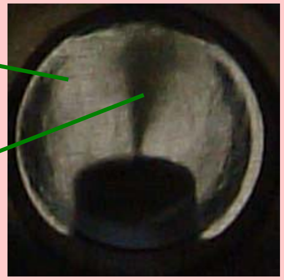


Ref: Kusdiana and Saka, 2004
Appl Biochem Biotech 115:781-791.

Direct Observation through Sapphire Window

MeOH

Oil



240.

280.

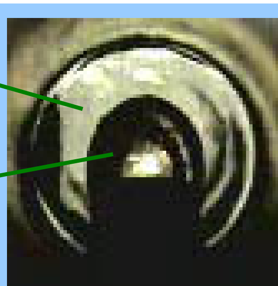
340.

Transesterification

2 Phase . 1 Phase
(Low Temp) (High Temp)

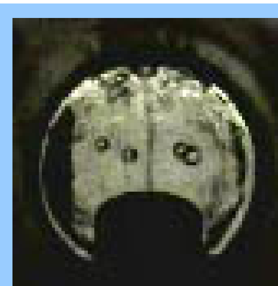
Water

Oil



280.

300.



340.

Hydrolysis

2 Phase . 2 Phase
(Low Temp) (High Temp)

MeOH
+
Fatty
Acid

160.

260.

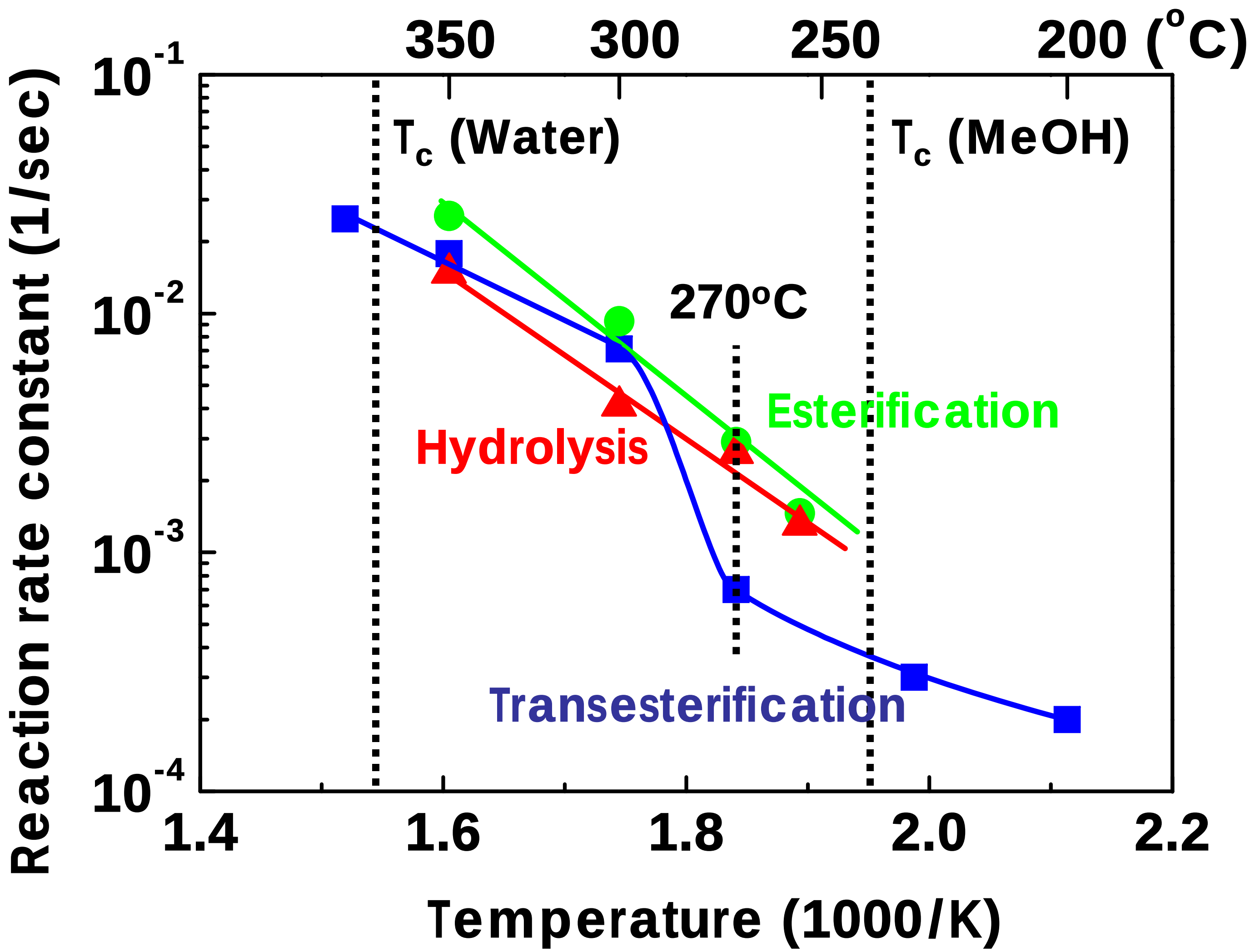
340.

Esterification

1 Phase . 1 Phase
(Low Temp) (High Temp)

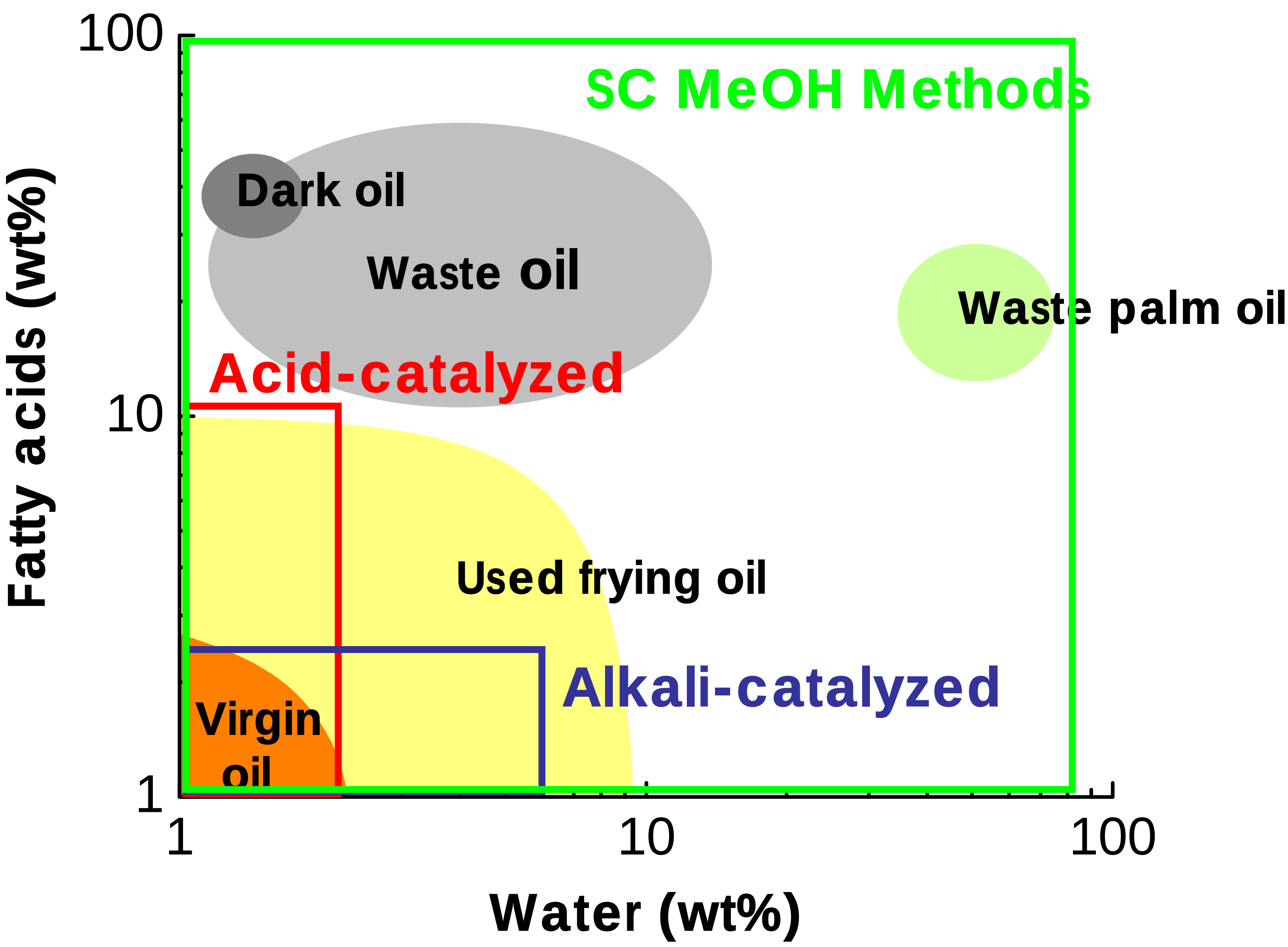
Ref: Kusdiana and Saka, 2004
Appl Biochem Biotech 115:781-791.

Arrhenius Plots for Transesterification, Hydrolysis and Esterification of Rapeseed Oil



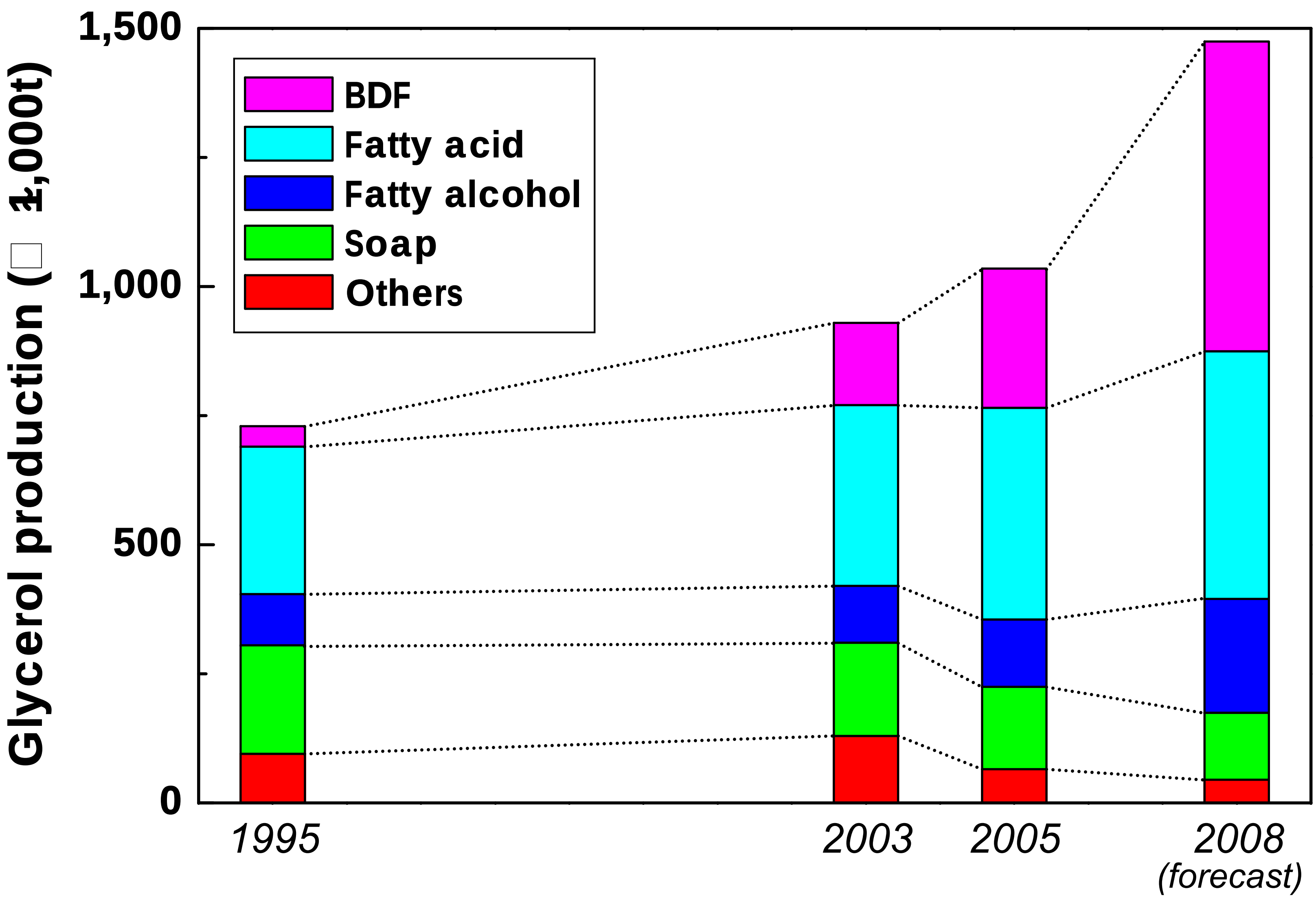
Ref: Kusdiana and Saka, 2004
Appl Biochem Biotech 115:781-791.

Applicable Range of Methods for Various Oils/Fats with different Water and Fatty Acid Contents



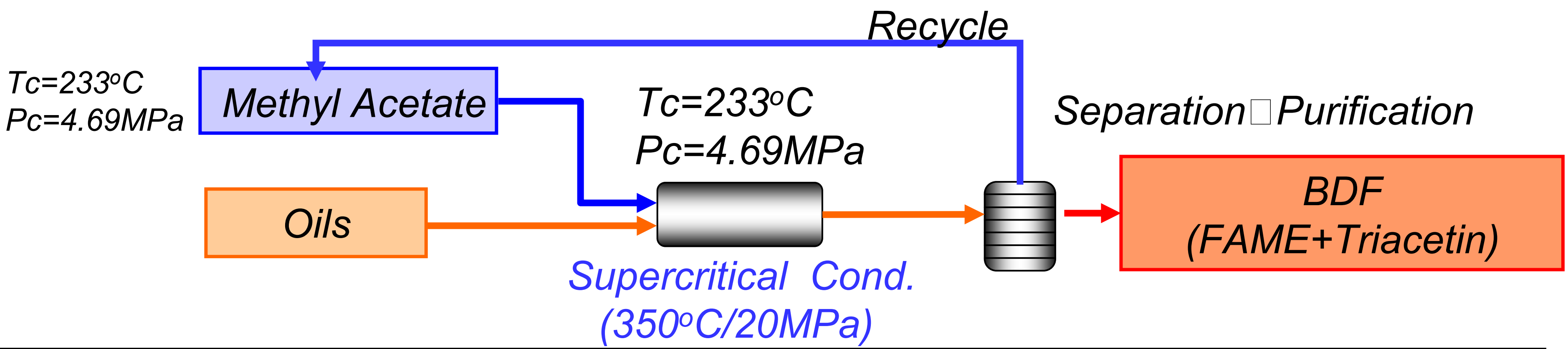
Ref: Saka, 2005
Japan Inst Energy 84:413-419.

Worldwide Glycerol Production



Ref: 2006, Yushi 59:24-25.

Biodiesel Production from Oils and Fats without Producing Glycerol by Carcoxylate Esters
-One-Step Supercritical Methyl Acetate Method-



Interesterification

CH_2□$OCOR^1$ / CH□$OCOR^2$ / CH_2□$OCOR^3$ (Triglyceride) + $3CH_3COOCH_3$ (Methyl Acetate) ⇒ (No catalyst) R^1COOCH_3 / R^2COOCH_3 / R^3COOCH_3 (FAME(BDF)) + CH_2□$OCOCH_3$ / CH□$OCOCH_3$ / CH_2□$OCOCH_3$ (Triacetin (BDF))

Esterification

R^4COOH (Fatty Acid) + CH_3COOCH_3 (Methyl Acetate) ⇒ (No catalyst) R^4COOCH_3 (FAME(BDF)) + CH_3COOH (Acetic Acid)

Ref: NEDO Pamphlet, p.21 (Oct 12,2007), Fuel in Press (2009)

Fuel Properties of Model Fuel and BDF Standards

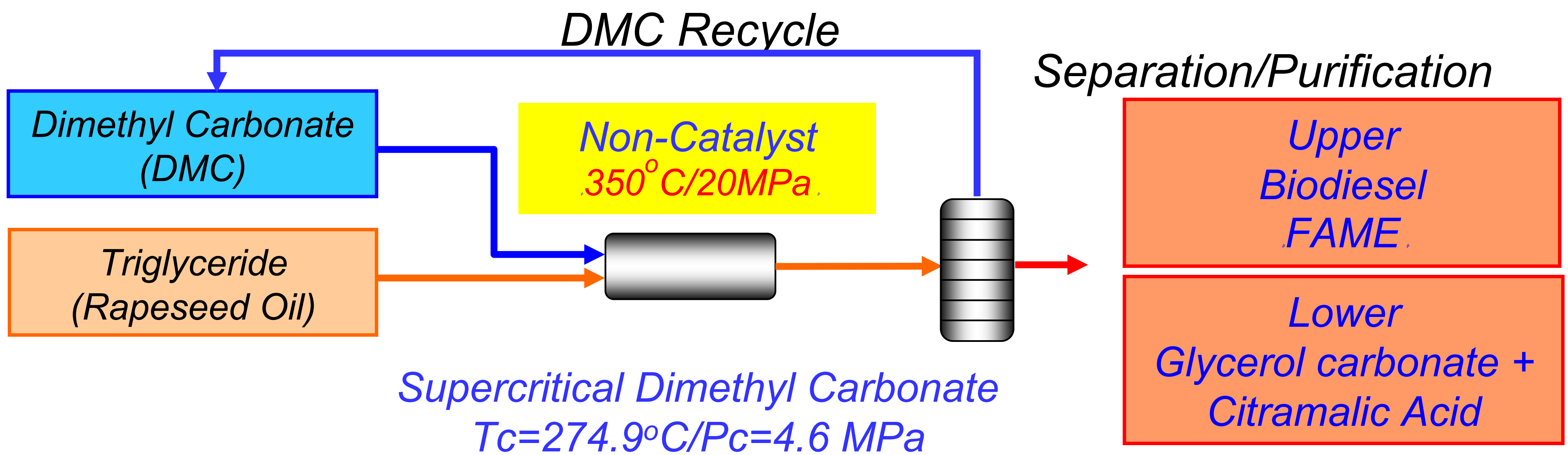
Properties	Unit	FAME	TA	Model BDF[a]	Kyoto	JASO[b]	EU	US
Density (15ºC)	g/ml	0.88	1.16	0.92	0.86 ~0.90	0.86 ~0.90	0.86 ~0.90	-
Kinematic viscosity (40ºC)	mm^2/s	4.4	7.3	4.5	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0
Cetane number	-	86.3	< 15	64.5	51	51	51	47
Carbon Residue (100%)	wt%	0.02	0.01	0.03	0.30 (10%)	0.30 (10%	0.30 (10%)	0.05
Pour point	ºC	-16.0	-40.0	-18.0	–7.5	-	-	-
Cold filter plugging point	ºC	-16.0	13.5	-17.0	–5	-	-	-
Flash point (closed cup)	ºC	170.5	158.5	154.5	100	120	101	> 130

[a] *Methyl Oleate/Triacetin□3:1 (mol/mol)*

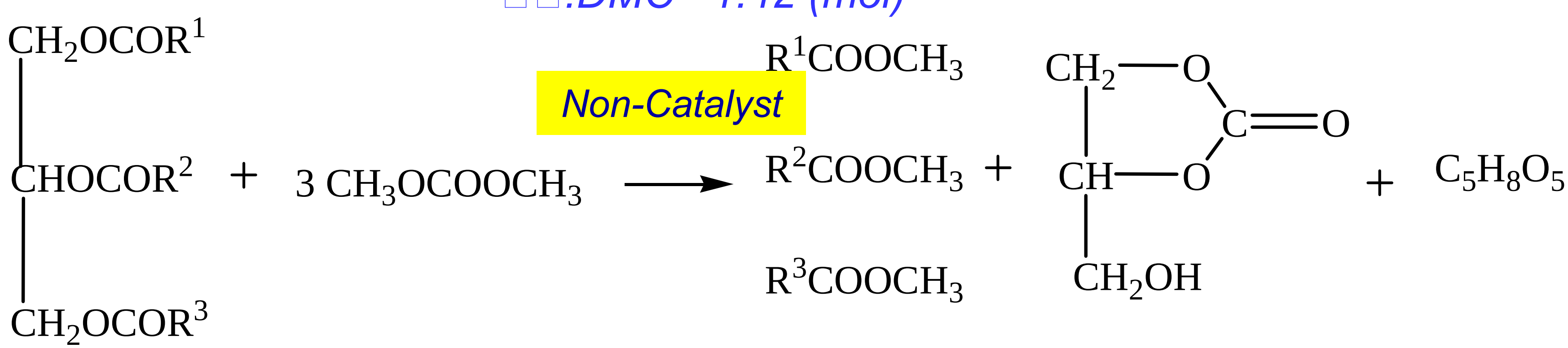
[b] *Japan Automobile Standards Organization□JASOStandard□Later JISStandard□JIS K2390□*

Fuel in Press (2009)

Biodiesel Production by Transesterification with Supercritical Dimethyl Carbonate



Supercritical Dimethyl Carbonate
Tc=274.9°C/Pc=4.6 MPa
□□:DMC= 1:42 (mol)

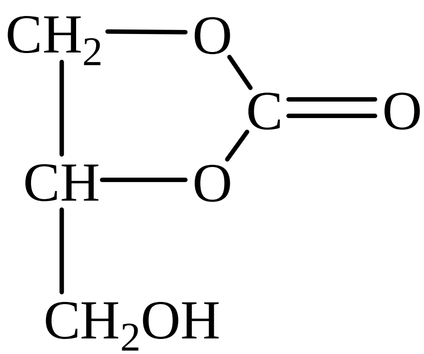


$$\begin{array}{l} CH_2OCOR^1 \\ | \\ CHOCOR^2 \\ | \\ CH_2OCOR^3 \end{array} + 3\ CH_3OCOOCH_3 \longrightarrow \begin{array}{l} R^1COOCH_3 \\ R^2COOCH_3 \\ R^3COOCH_3 \end{array} + \text{Glycerol carbonate} + C_5H_8O_5$$

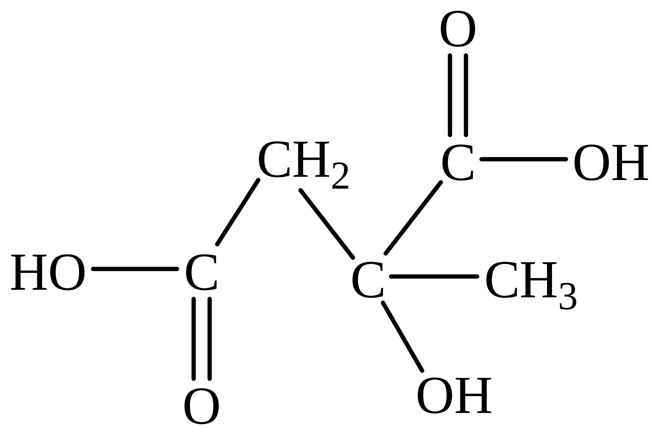
Triglyceride | **Dimethyl carbonate** | **Fatty acid methyl ester** | **Glycerol carbonate** | **Citramalic Acid**

Ref: Ilham and Ehara, 2009
Biores Technol 100:1793-1796.

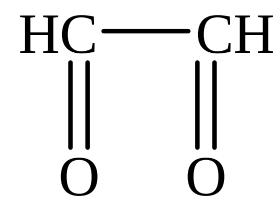
By-Products of Biodiesel Produced by Supercritical Dimethyl Carbonate



Glycerol Carbonate



Citramalic Acid



Glyoxal

- *Solvents for paints, dyes and adhesives.*
- *New source of polymeric materials.*
- *Cosmetic and dermatologic.*
- *Emulsifier*

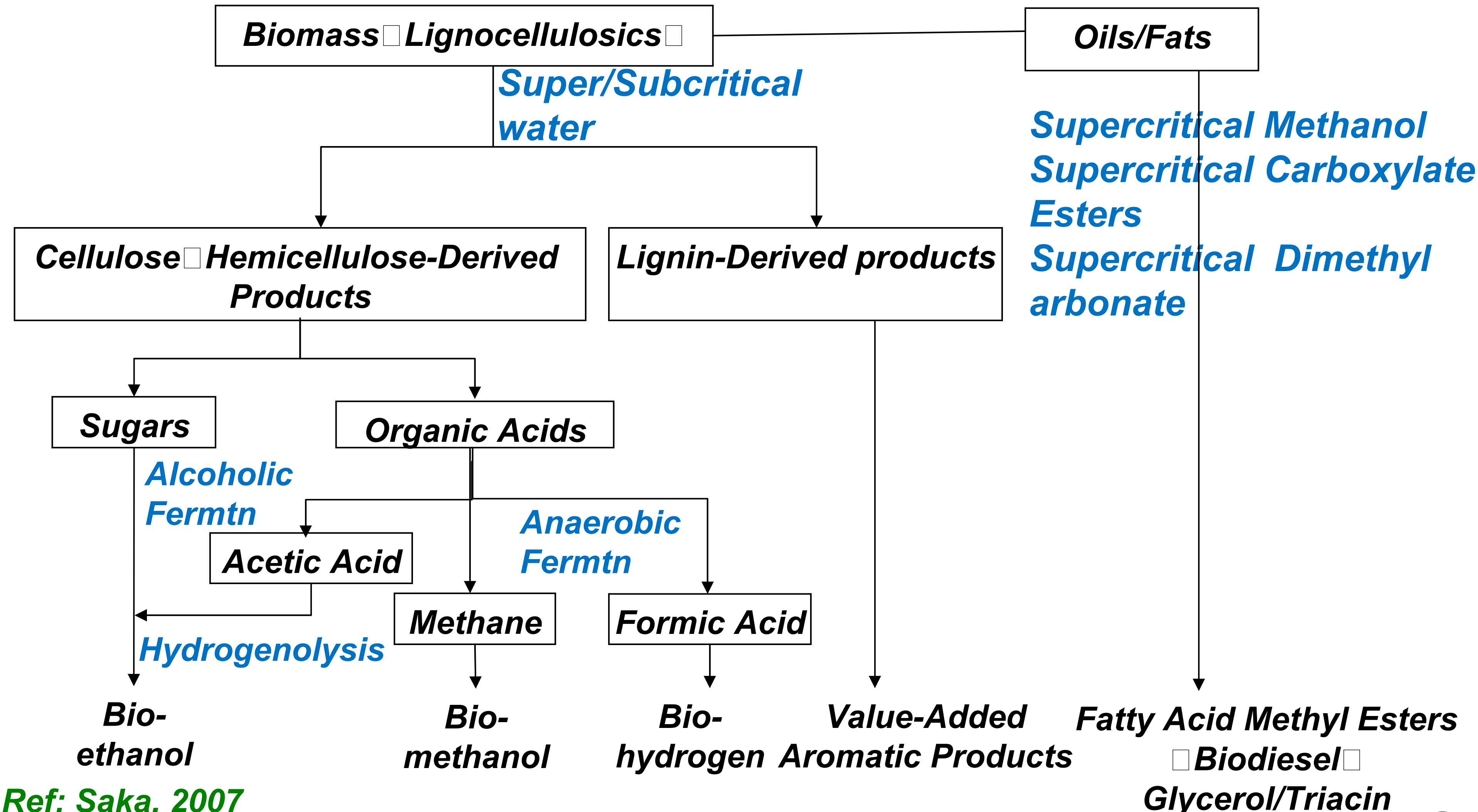
- *Pharmaceutical applications.*

- *Printing.*
- *Textile dyeing.*
- *Rust and scale removal.*

(Cheol et al., 2003,2004; Rolf et al., 2000; Joerg et al., 1999; Ruey et al., 1997; Kiyoura and Kogure, 1997)

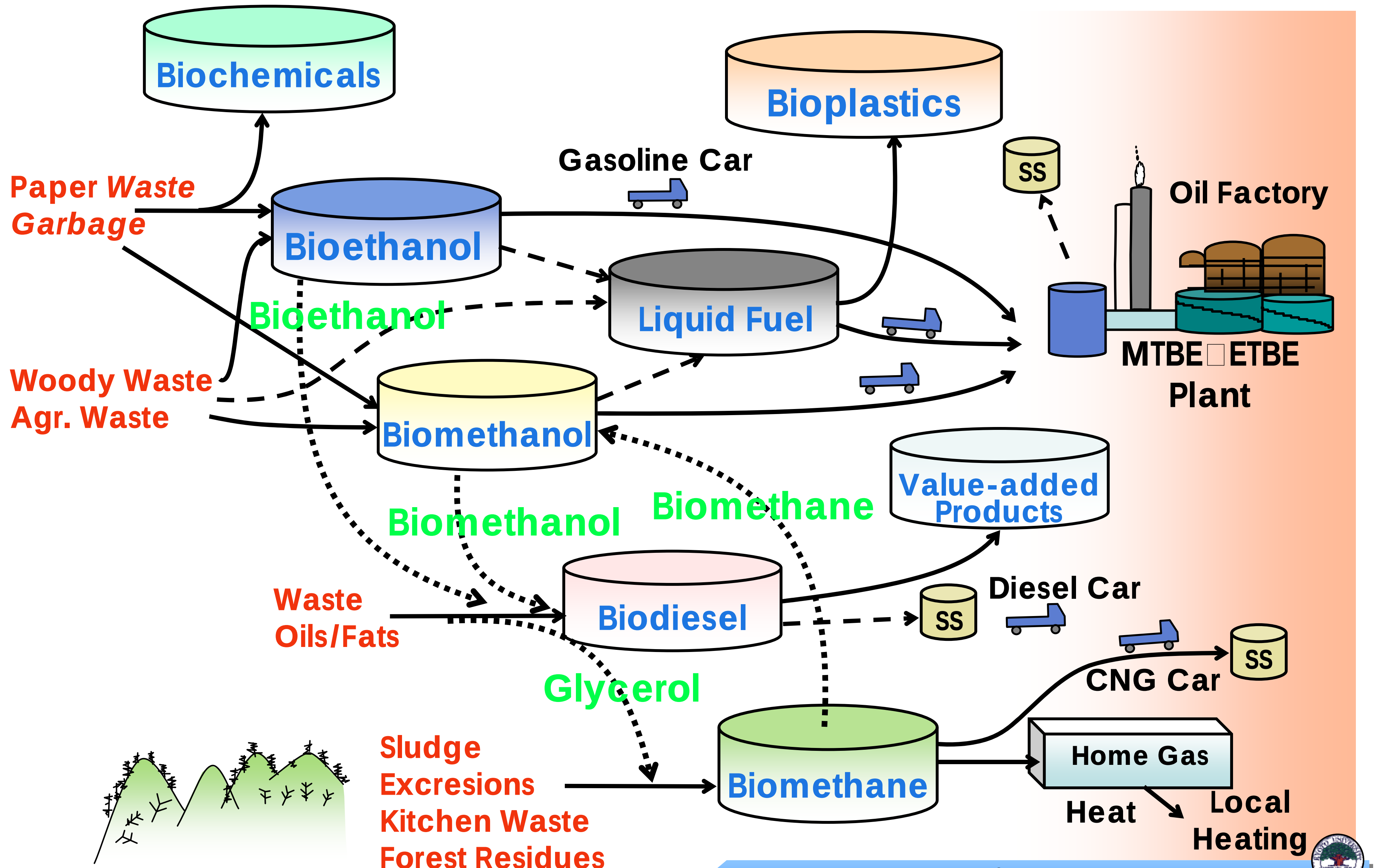
Ref: Ilham and Ehara, 2009 Biores Technol 100:1793-1796.

Biofuels and Biochemicals from lignocellulosics by Supercritical Fluid Technologies



Ref: Saka, 2007
Ad Tech for Chem from Wood Res
p.56, CMC Publisher.

Zero-Emission Type Biorefinery for Chemicals and Bioenergy and its Utilization System



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Members of Saka's Laboratory

Acknowledgements

Thank you for your kind attention!

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