QIBEBT

Biochemicals and biofules from lignocellulose via catalytic conversion

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中国科学院青岛生物能源与过程研究所

Outlines

1. Renewable energy utilization in China
2. Lignin depolymerization
3. Hydrodeoxygenation of bio-oils
4. Biochemicals from biomass

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QIBEBT

Renewable energy sources

Solar energy

Wind

Hydroenergy

Ocean energy

Geothermal

Biomass

Renewable energy sources

Solar energy | Wind | Hydroenergy

- 《World Energy Outlook 2017》: Over the next 20 years, China will be the largest source of renewable energy growth.
- From 2016 to 2020 (the 13th Five Year Plan), the total investment on renewable energy will reach 2.5 trillion RMB in China, the development and utilization of renewable energy will greatly improve the environment problems.
- Xiong-An New Area will be established on the basis of clean and renewable energy.
- By the end of 2016, Shandong province has new energy and renewable energy installed capacity of 15.805 GW, accounting for 14.4% of the total electricity generating.

Renewable energy sources

Compete the goals of the 12th Five-Year Plan

Hydroelectricity 320 GW

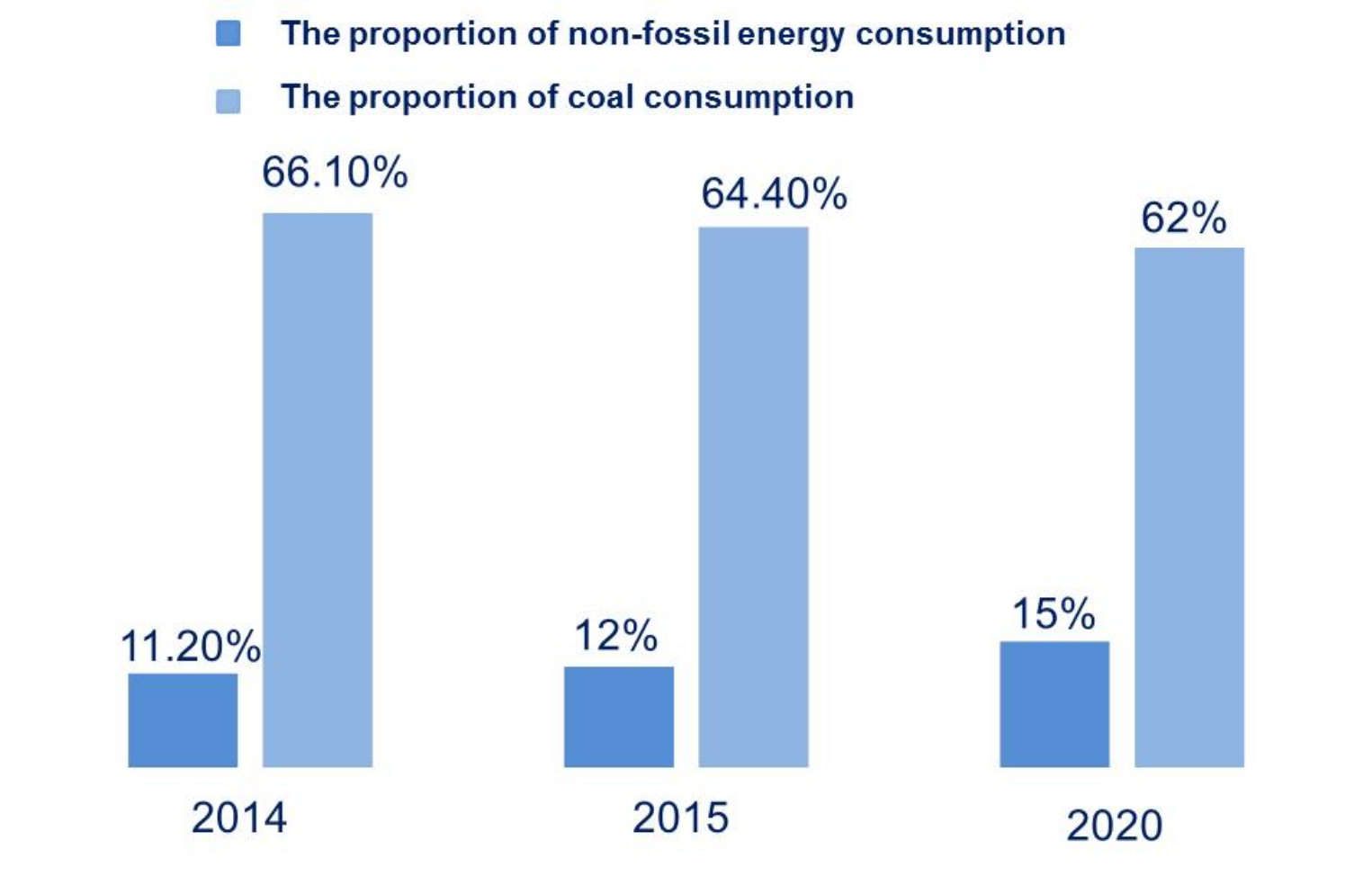
Wind power 120 GW

Photovoltaic power 40 GW

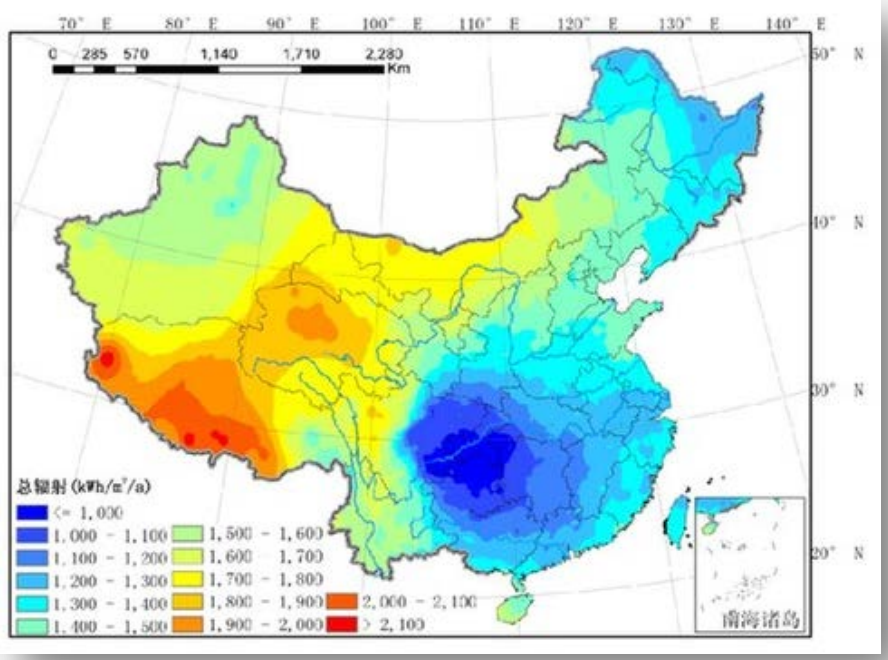
Renewable resources 32.7%

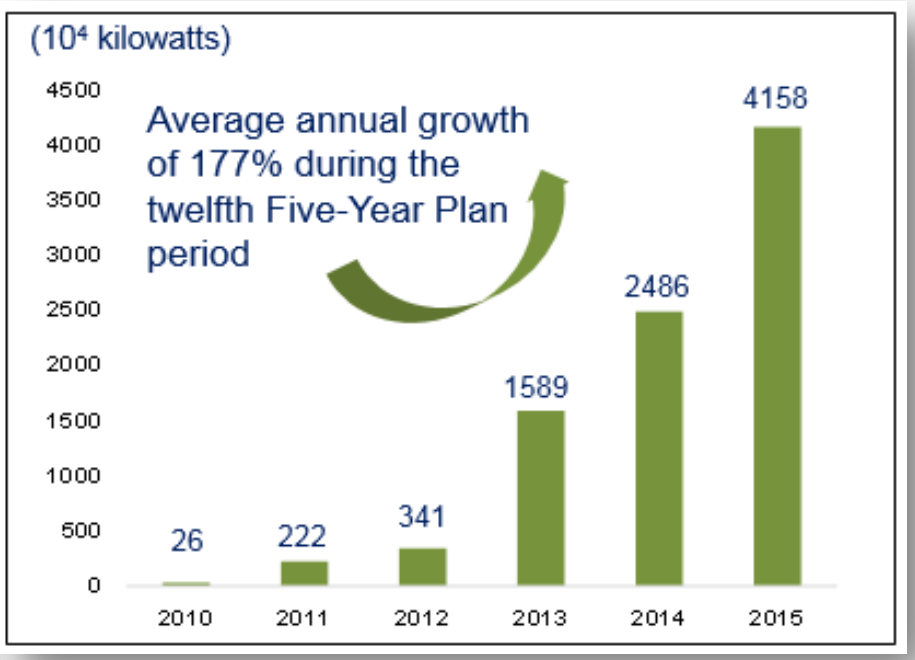
Energy structure adjustment

The coal consumption ratio continued to decline



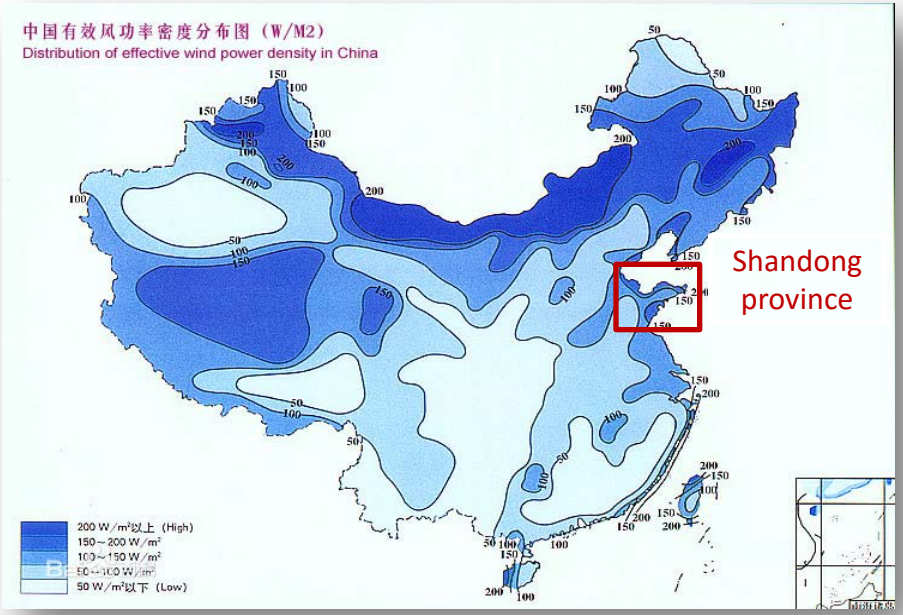
Photovoltaic power generation





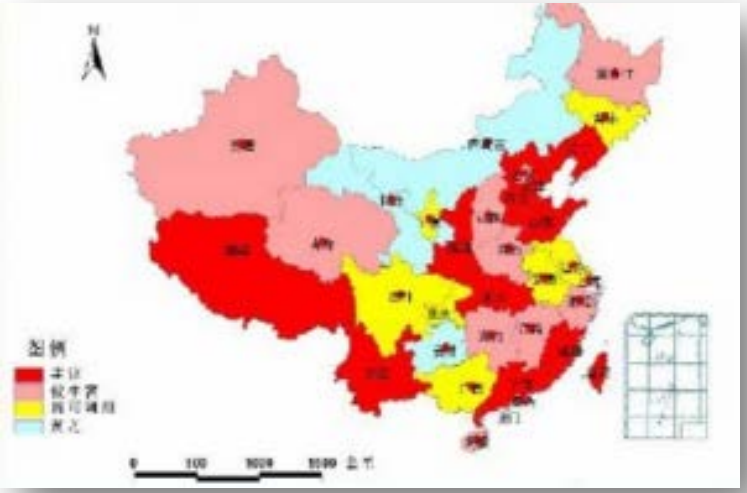
By the end of 2016, the cumulative photovoltaic installed capacity in China has reached 43.18 GW, growing to be the largest in the world.

Wind power distribution

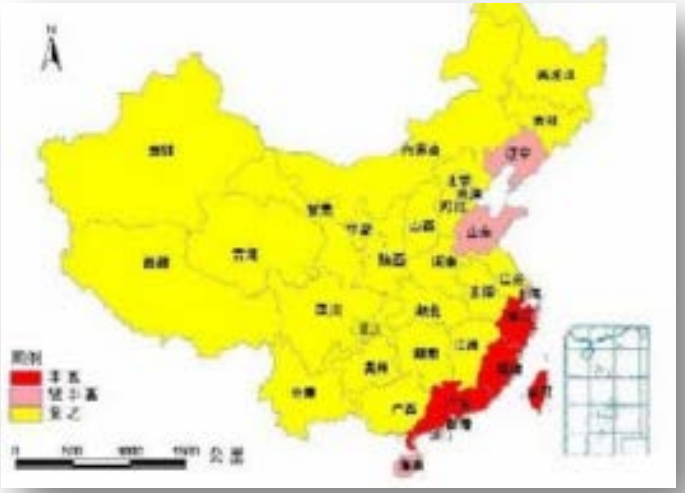


By 2020, the wind power installed capacity of Shandong province will reach 14 GW, accounts for the proportion of 8.6% of the total electricity generating.

Geothermal and ocean energy distribution



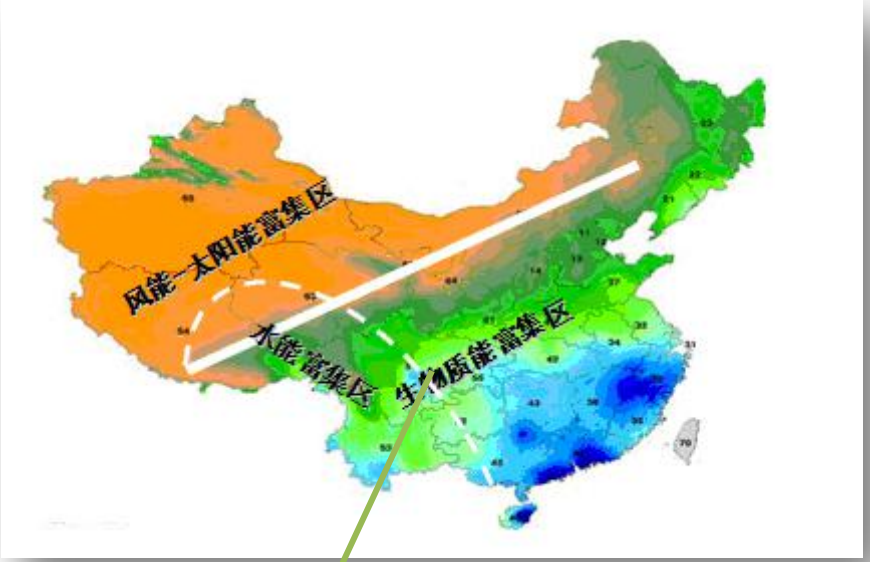
Geothermal resources distribution



Ocean energy distribution

Geothermal resources: Widely distributed
Ocean energy: Littoral

Biomass energy



Biomass enrichment region

There are abundant biomass resources in China, 70% of rural energy comes from biomass. More than 600 million tons of crop stalks are generated every year.

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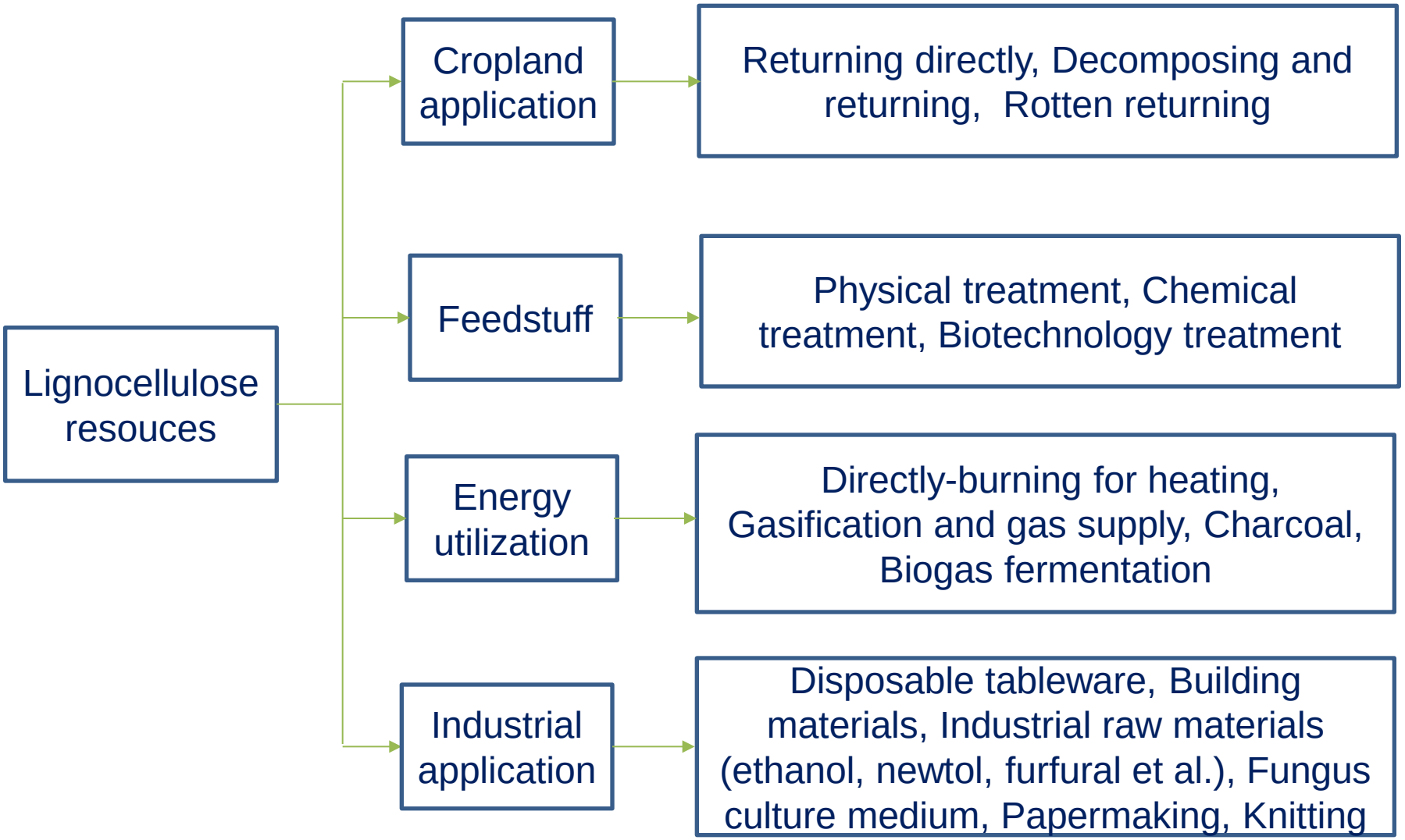
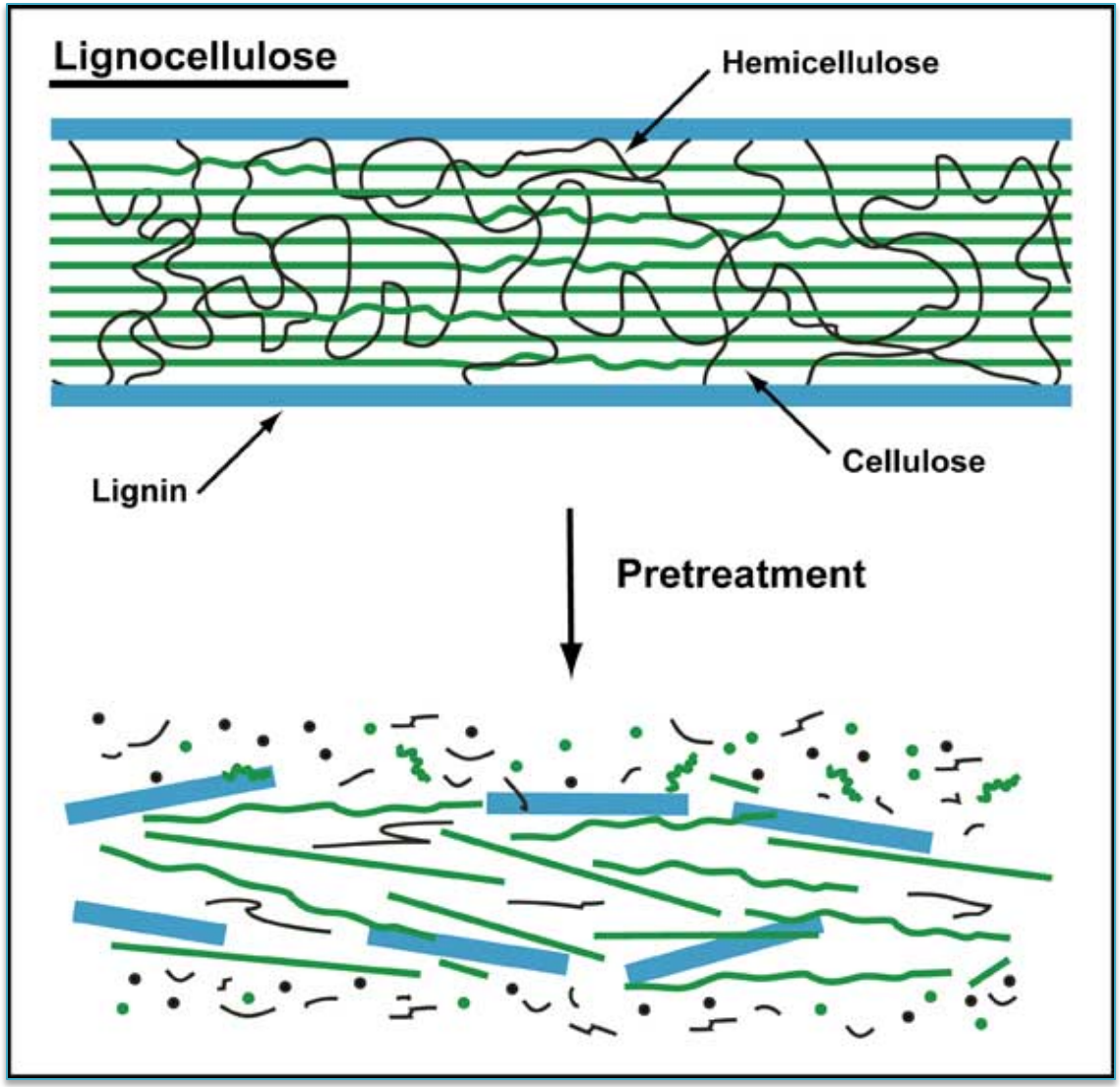
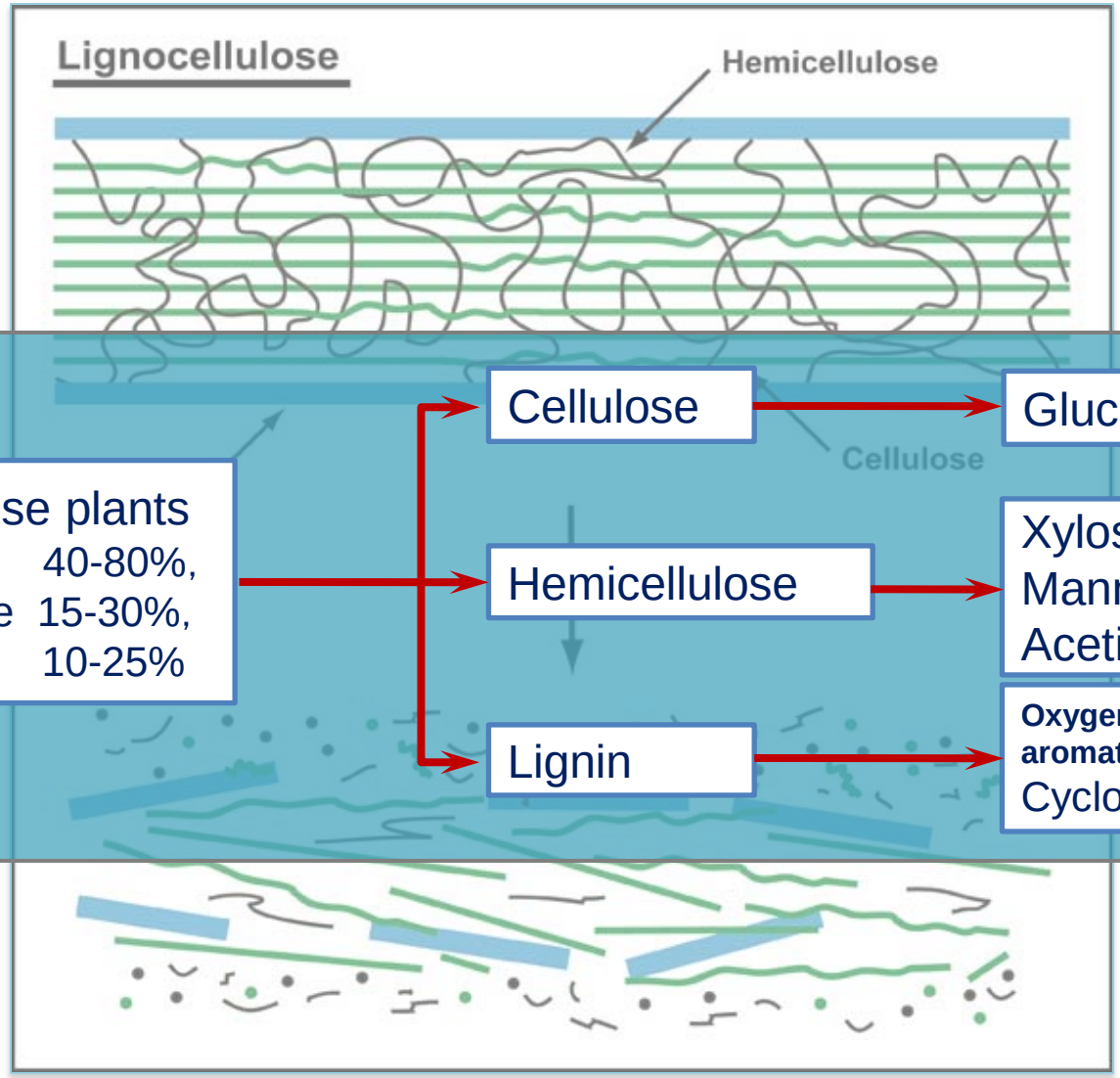
Biomass application



Lignocellulose



Lignocellulose



Lignocellulose plants
Cellulose 40-80%,
Hemicellulose 15-30%,
Lignin 10-25%

Cellulose → Glucose

Hemicellulose → Xylose, Mannose, Acetic acid

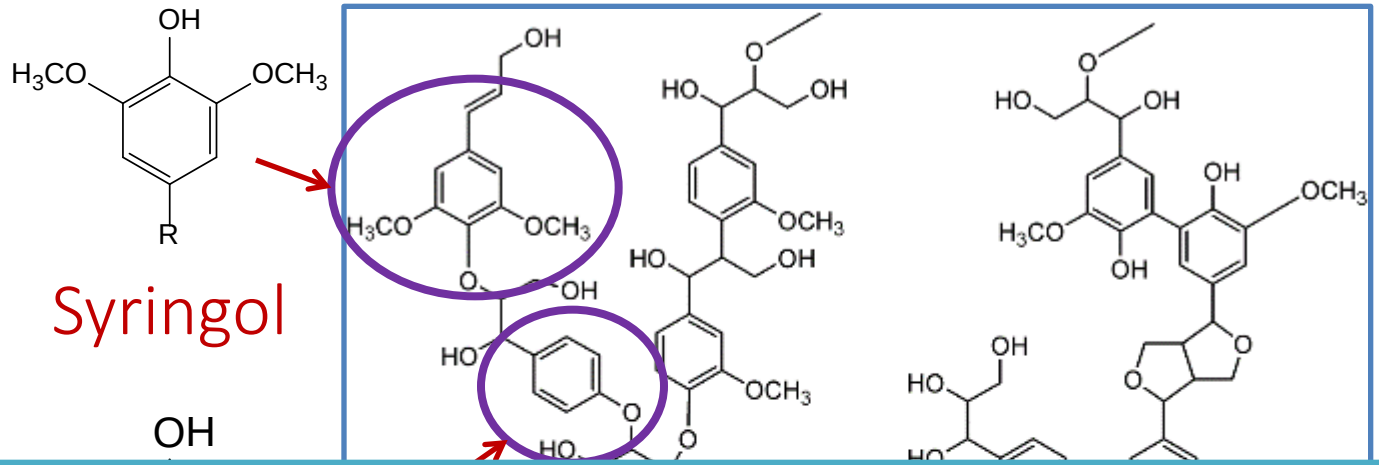
Lignin → **Oxygen containing aromatic hydrocarbons,** Cycloalkanes

Lignin

Cellulose utilization

Lignin

Lignin



- Lignin is a cross-linked amorphous copolymer with random polymerized structure of the three primary phenylpropane monomers (syringyl (S), guaiacyl (G) and p-hydroxyphenyl units (H)), which are bonded together through several different C–O–C and C–C interunit linkages.
- The energy density of lignin is 30% greater than that of polysaccharide polymers and it is one of the few natural large-scale sources of aromatic compounds

Lignin depolymerization Backgound

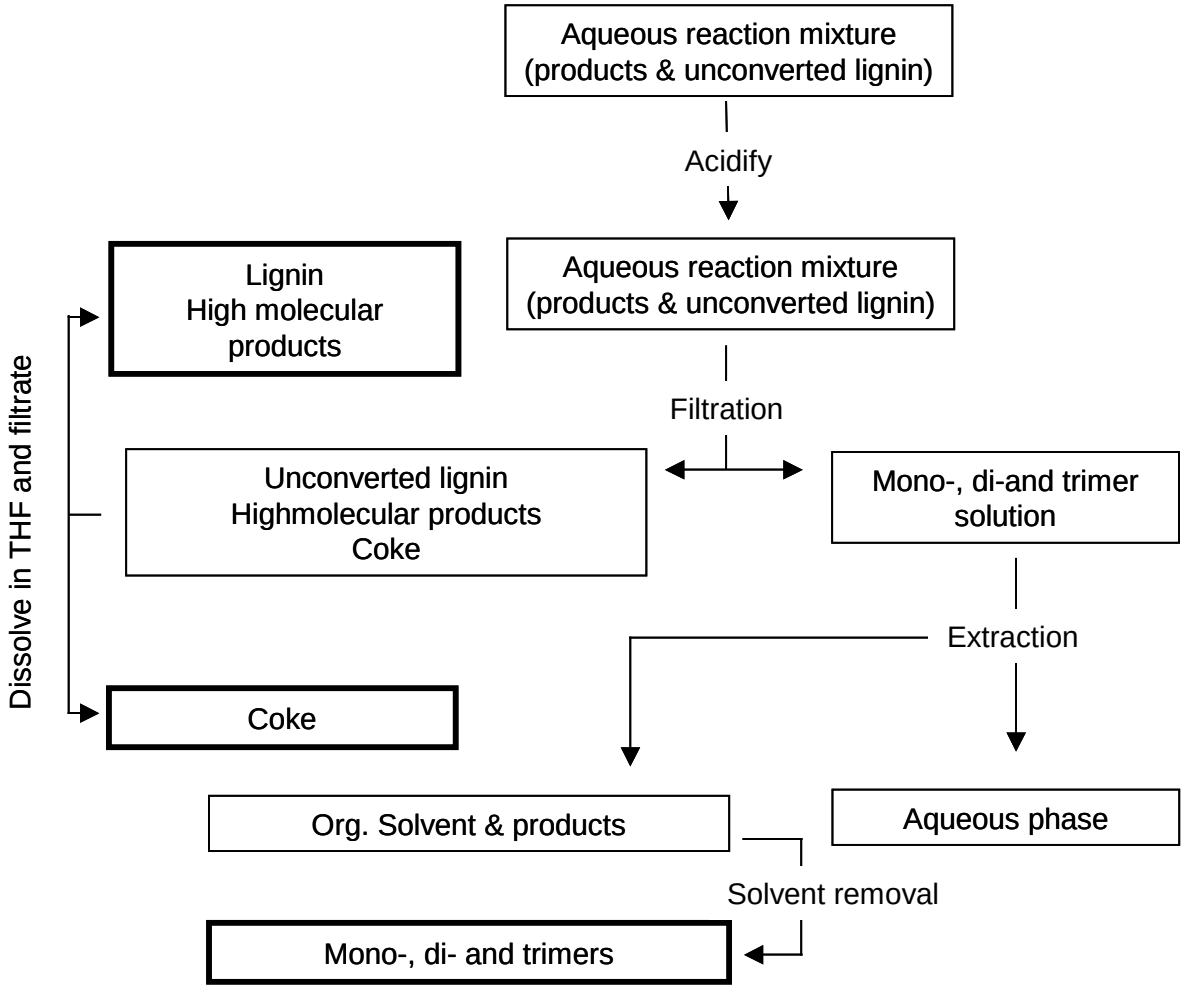
Depolymerization by alkaline organosolv

Depolymerization in supercritical water

Not exceed yields of approximately 20 -23 wt.% of product oil

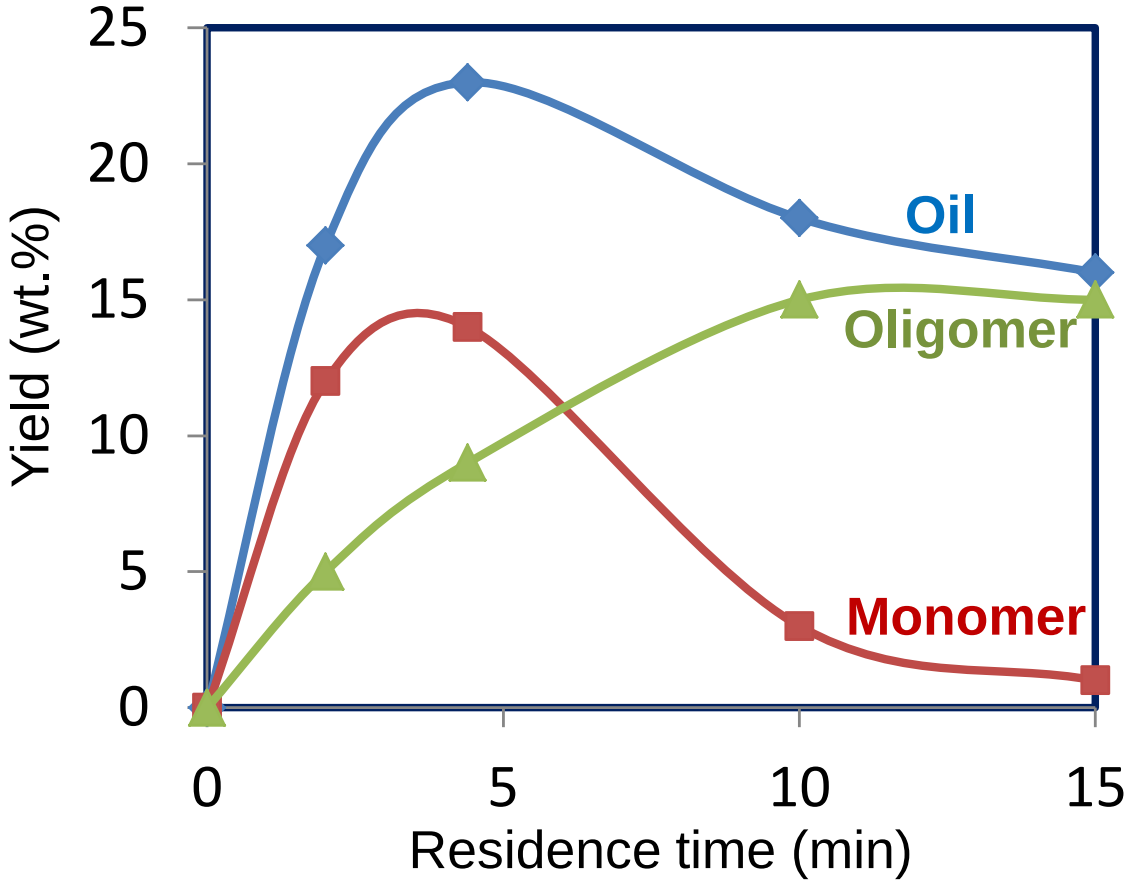
- The re-polymerization of the highly reactive products with formation of higher molecular compounds, defined as unconverted lignin.
- CHN analysis of the above unconverted lignin showed a different chemical composition than the original lignin.

Lignin depolymerization Product isolation



Virginia M. Roberts, Valentin Stein, Thomas Reiner, Angeliki Lemonidou, **Xuebing Li,** Johannes A. Lercher
Towards quantitative catalytic lignin depolymerization. Chem. - Eur. J. 17 (2011) 5939−5948.

Lignin depolymerization Effct of time

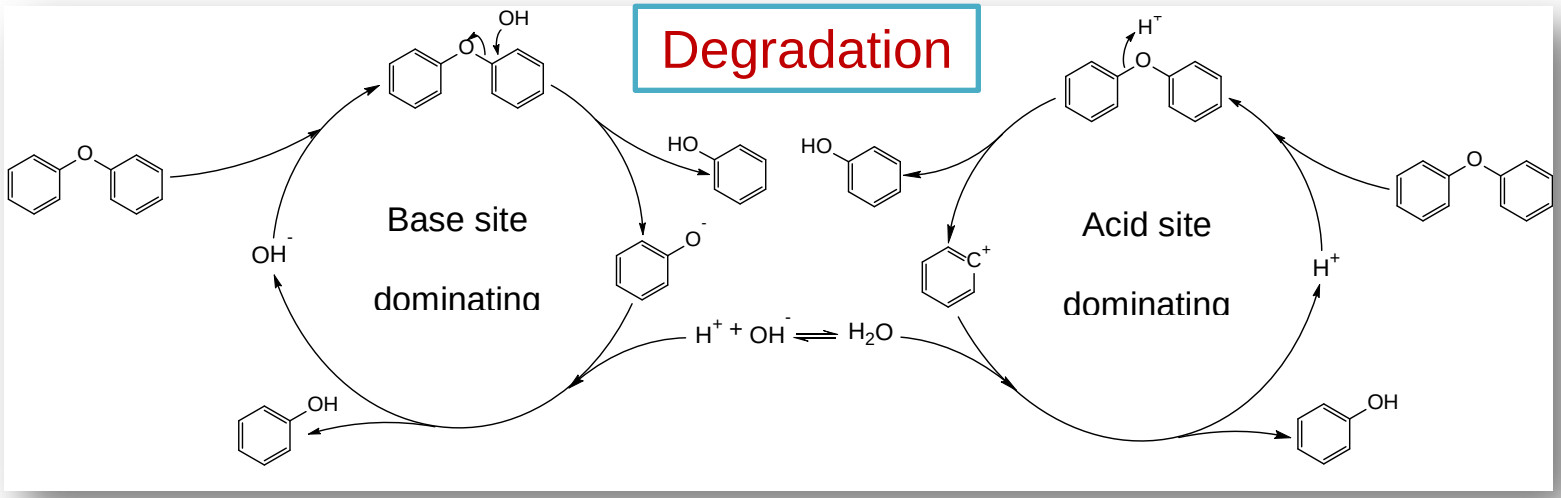


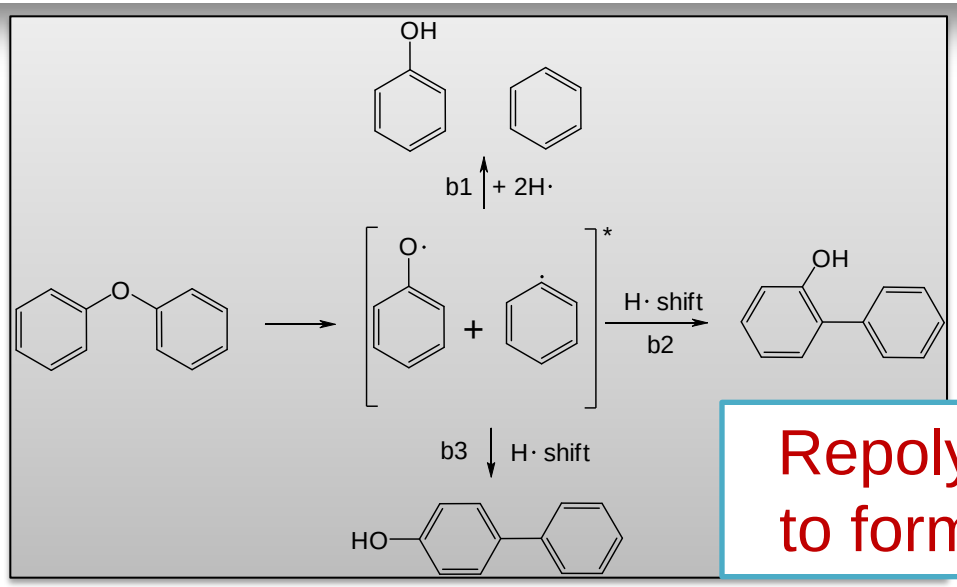
300 °C and 250 bar, 10 wt.% lignin in 4 wt.% NaOH solution

Lignin depolymerization Monomer

Monomer	Chemical formula	Conc.[wt.%]
Syringol	**$C_8H_{10}O_3$**	**40.9**
Syringyl aldehyde	**$C_9H_{10}O_4$**	**18.0**
3, 5-dimethoxy-4-hydroxy acetophenone	**$C_{10}H_{12}O_4$**	**16.3**
4-methyl-syringol	**$C_9H_{12}O_3$**	**6.7**
Guaiacol	**$C_7H_8O_2$**	**10.5**
Vanillin	$C_8H_8O_3$	3.5
4-hydroxy-3-methoxy phenylacetone	$C_{10}H_{12}O_3$	2.3
Ortho-methoxy-catechol	$C_7H_8O_3$	1.6

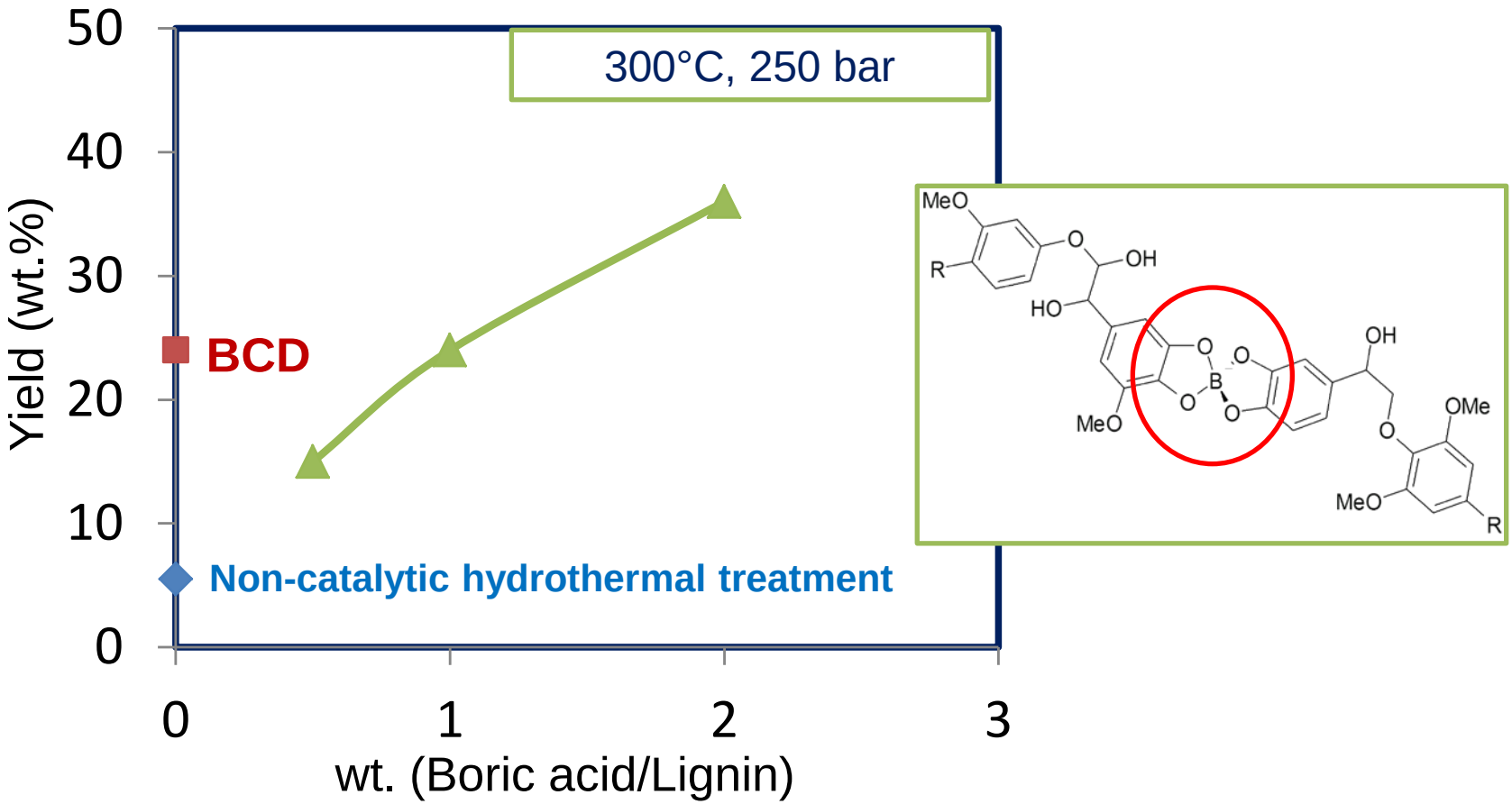
Lignin depolymerization Repolymerization





Repolymerization to form C-C bond

Lignin depolymerization Boric acid system



Lignin depolymerization Boric acid system

wt. (NaOH/Boric acid)	pH	Oil Yield (wt.%)
0	3.5	36
0.50	9.6	29
0.75	13.0	52
1.00	13.3	47
1.25	13.4	29

The extraction of the filter cake exhibited very similar product distribution as the oil, and led to oil yield as high as 85 wt.%.

Lignin depolymerization Methylation

Methylation of active hydroxyl in lignin

+

Methylated lignin depolymerization on solid base catalyst

→ Bio-oils

Conversion=100 %

Conversion > 90 %

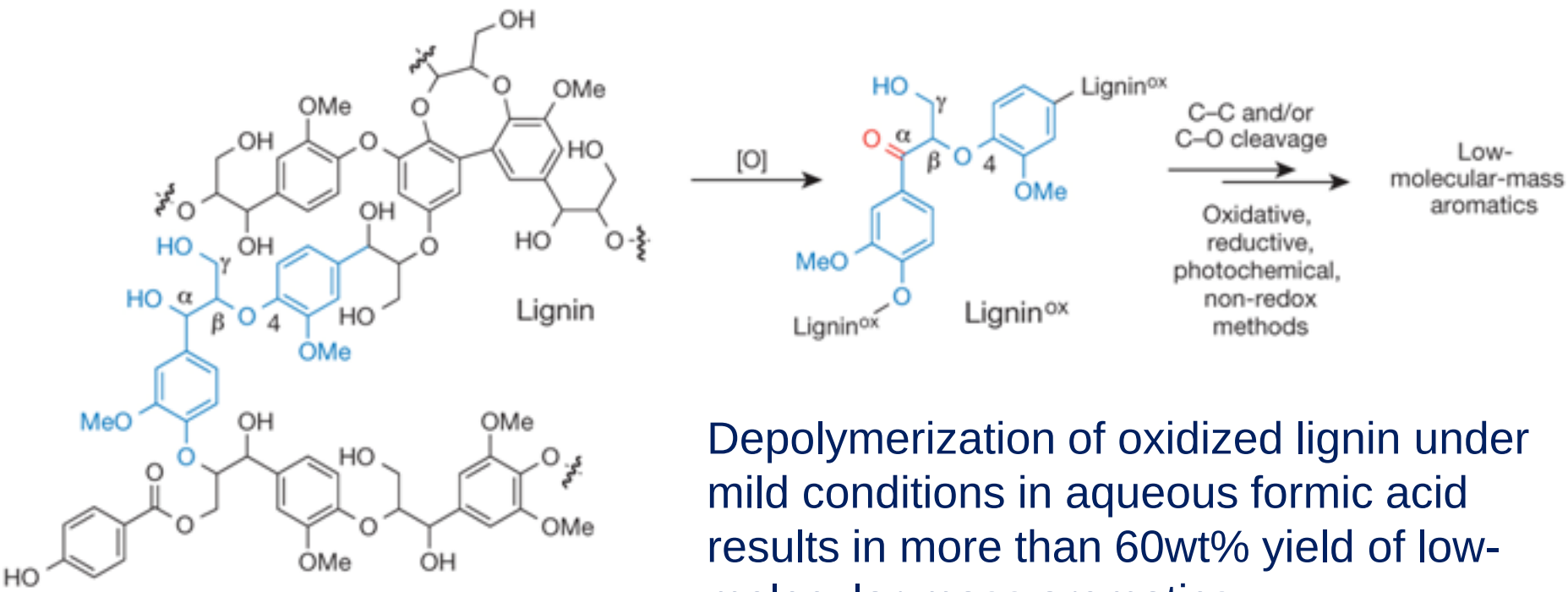
Methylation: DMC

Lignin: Organosolv lignin
Catalyst: 10 wt%Ni-MgO/Al_2O_3
H_2 source: H_2
Solvent: Water, Ethanol, Dodecane

A Highly Efficient, Green, and Cheap Depolymerization Process.

Funded by National natural Science Foundation of China:21676287

Lignin depolymerization Oxidation



Depolymerization of oxidized lignin under mild conditions in aqueous formic acid results in more than 60wt% yield of low-molecular-mass aromatics.

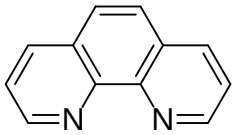
A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature*, **2014**, 515, 249-252.

Lignin depolymerization Ozonation

Oxidation system

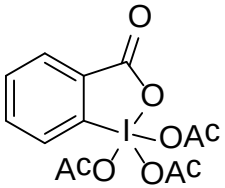
CrO_3 + H_2SO_4

$Fe(acac)_3/phen/K_2CO_3/NaOH$

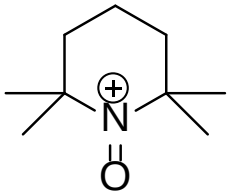


phen

Dess-Martin periodinane



DMP



HCl HNO_3

4-acetamido-TEMPO

O_3 Green, cheap and efficient

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Hydrodeoxygenation of bio-oil Background

30% of water

Unstable

HDO with cobalt or nickel doped molybdenum sulfides

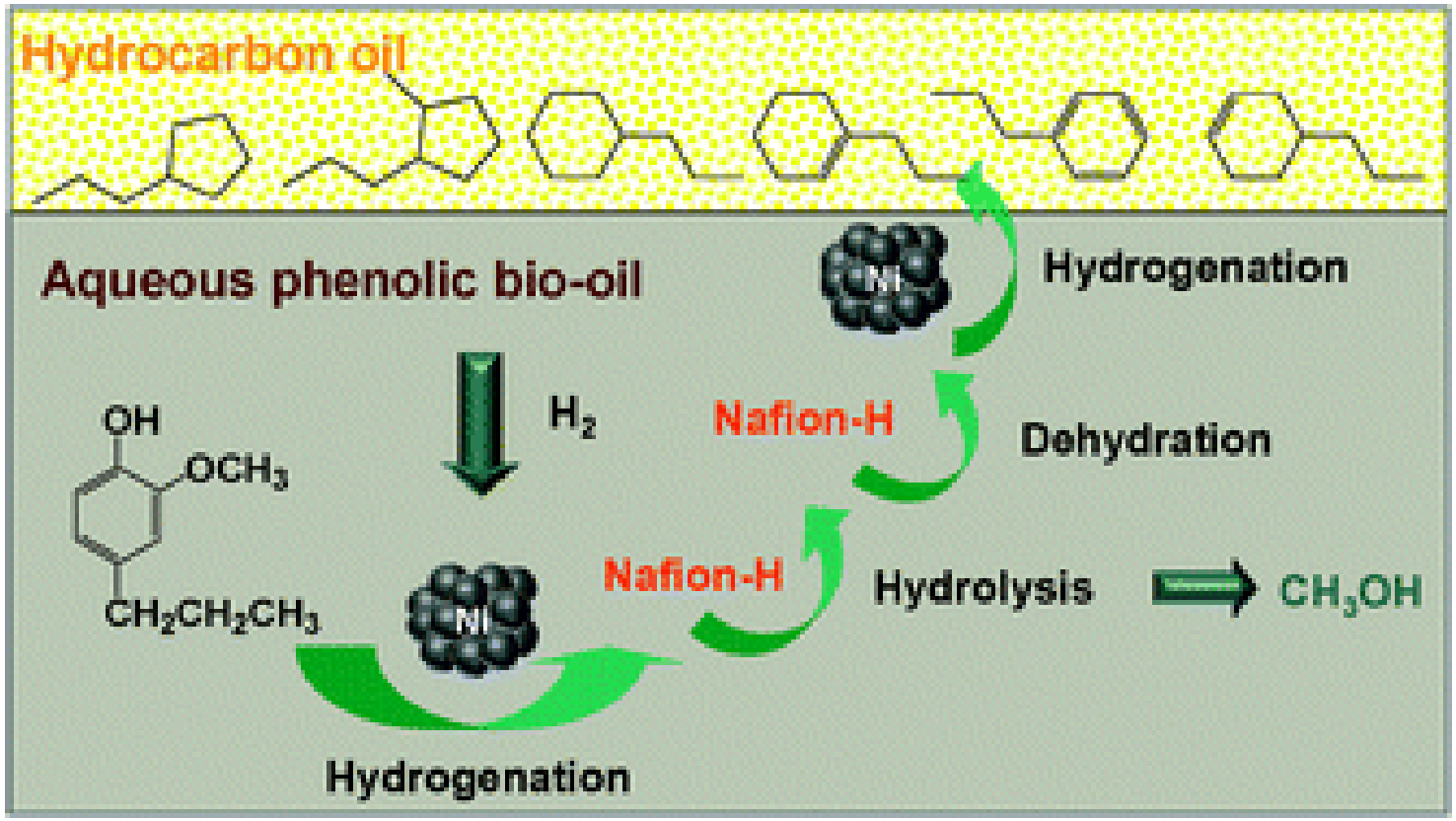
Sensitive to water，poisoned by the oxygen containing compounds

Cracking by zeolitic catalysts at 400 ^{o}C

The oxygenates are mostly converted to carbonaceous deposits

?

Hydrodeoxygenation of bio-oil In aqueous sulution

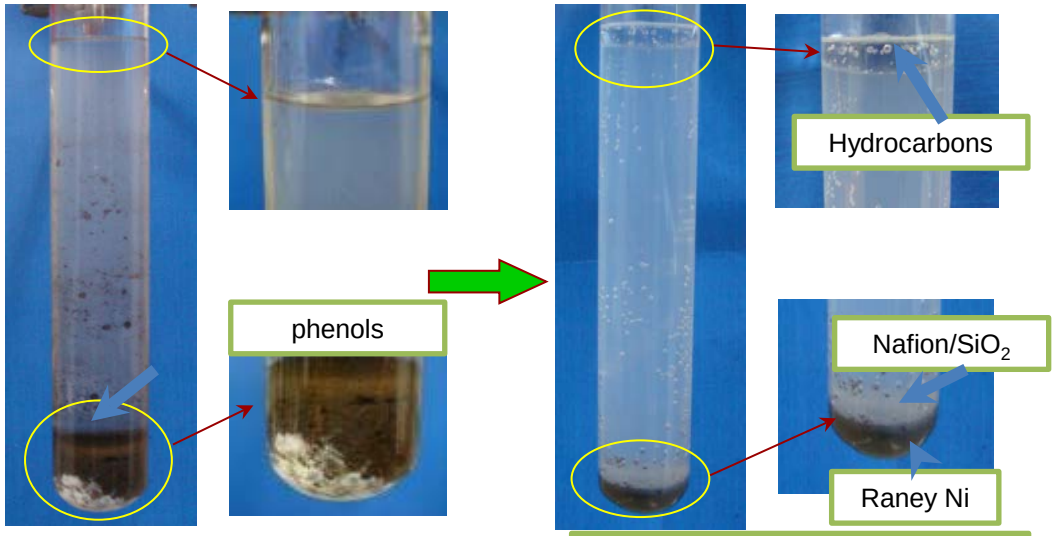


By benzene hydrogenation, ether bond hydrolysis and alcohol dehydration, bio-oil derived from lignin depolymerization are transformed into cycloalkanes, which are isolated from water automatically.

Hydrodeoxygenation of bio-oil Bifunctional catalysts

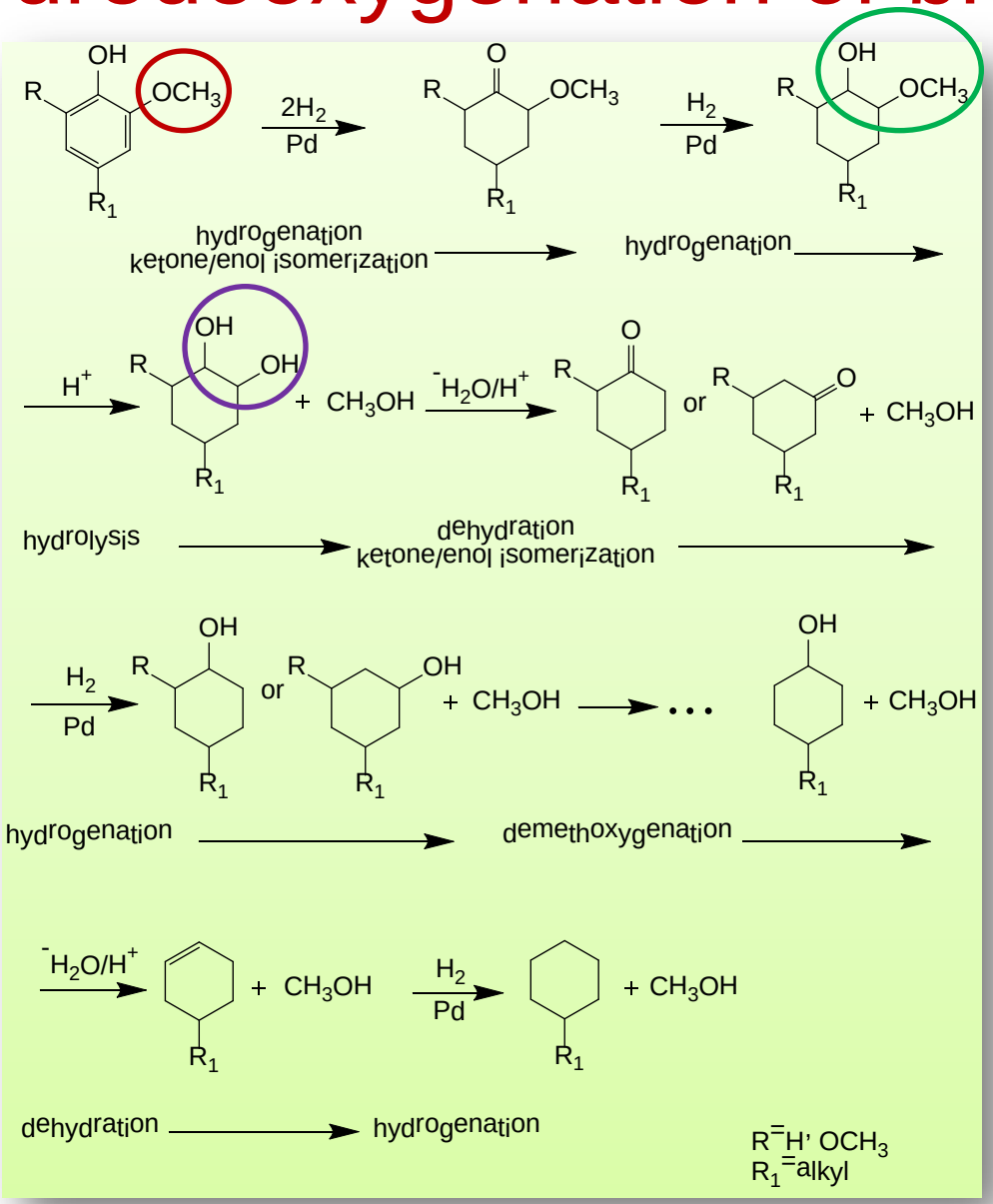
Bifunctional catalysts

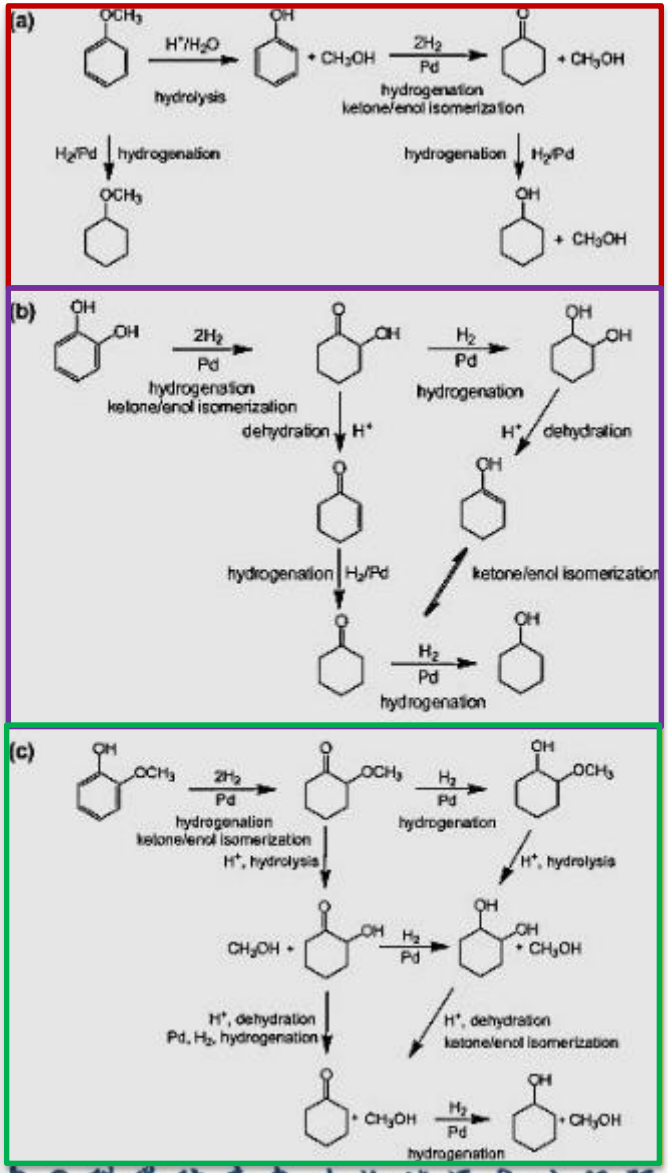
- **Hydrogenation catalysts**
  - Noble metal: Pt/C, Pd/C, Ru/C
  - Non-noble metal: Raney Ni, Ni-doped catalysts
- **Hydrolysis and the dehydration catalysts**
  - Mineral acid: Phosphoric acid ; Sulfuric acid
  - Organic acid: Acetic acid
  - Solid acid: Nafion, Zeolite



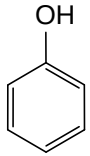
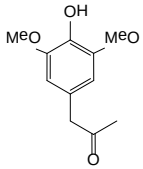
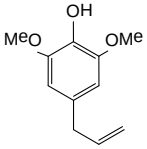
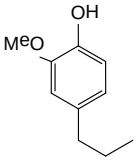
(A) Before reaction (B) After reaction

Hydrodeoxygenation of bio-oil Bifunctional catalysts





Hydrodeoxygenation of bio-oil Bifunctional catalysts

Catalyst	Reactant	Reaction conditions	Conversion (%)	Selectivity to cycloalkanes (%)
Pd/C; H_3PO_3		5 MPa H_2, 523 K, 0.5 h	100	98
Pd/C; H_3PO_3		5 MPa H_2, 523 K, 0.5 h	100	80
Pd/C; HZSM-5		5 MPa H_2, 473 K, 2 h	95	80
RANEY Ni Nafion/SiO_2		4 MPa H_2, 573 K, 0.5 h	80	86

Note that HZSM-5 showed a high rate of dehydration (1600 mol mol-$[H^+]^{-1}$ h^{-1}), two orders of magnitude higher than that of H_3PO_4 (15 mol mol-$[H^+]^{-1}$ h^{-1}).

Hydrodeoxygenation of bio-oil Bifunctional catalysts

The mechanisms of outstanding dehydration and hydrolysis of acidic zeolite：

•The accumulation effect of zeolite could increase the concentration of reactants, therefore promoting the catalytic reaction.

•The pores of zeolite are suitable for reactants transporting to the acid sites, promoting the equilibrium reaction from alcohol monomer/oligomer to monomer with high reactivity.

V. M. Roberts, V. Stein, T. Reiner, A. A. Lemonidou, **X. Li**, J.A. Lercher, *Chem. Eur. J.* 17 (2011) 5939;
V. M. Roberts, R. T. Knapp, **X. Li**, J.A. Lercher, *ChemCatChem* 2 (2010) 1407;
V. M. Roberts, S. Fendt, A.A. Lemonidou, **X. Li**, J.A. Lercher, *Appl. Cat. B* 95 (2010) 71*;*
C. Zhao, Y. Kou, A.A. Lemonidou, **X. Li**, J.A. Lercher, *Chem. Comm.* 46 (2010) 412*;*
C. Zhao, Y. Kou, A.A. Lemonidou, **X. Li**, J.A. Lercher, *Angew. Chem. Int. Ed.* 48 (2009) 3987;
C. Zhao, J. He, A. A. Lemonidou, **X. Li**, J. A. Lercher, *J. Catal*. 280 (2011) 8;
C. Zhao, J. A. Lercher, *ChemCatChem* 4 (2012) 64;
C. Zhao, J. A. Lercher, *Angew. Chem. Int. Ed*. 51 (2012) 5935.

C. Zhang, J. Xing, L. Song, H. Xin, S. Lin, L. Xing, **X. Li***, *Catal. Today* 234 (2014) 145.
X. Li, J. Xing, M. Zhou, H. Zhang, H. Huang, C. Zhang, L. Song*, **X. Li***, *Catal. Commun.* 56 (2014)123.
J. Xing, L. Song, C. Zhang, M. Zhou, L. Yue, **X. Li***, *Catal. Today* 258 (2015) 90.
C. Zhang, J. Qi, J. Xing, S. Tang, L. Song, Y. Sun, C. Zhang, H. Xin, **X. Li*,** RSC Adv. 6 (2016) 104398.
J. Qi, X. Sun, S. Tang, Y. Sun, C. Xu, X. Li, **X. Li***, *Appl. Catal. A-Gen.* 535 (2017) 24.

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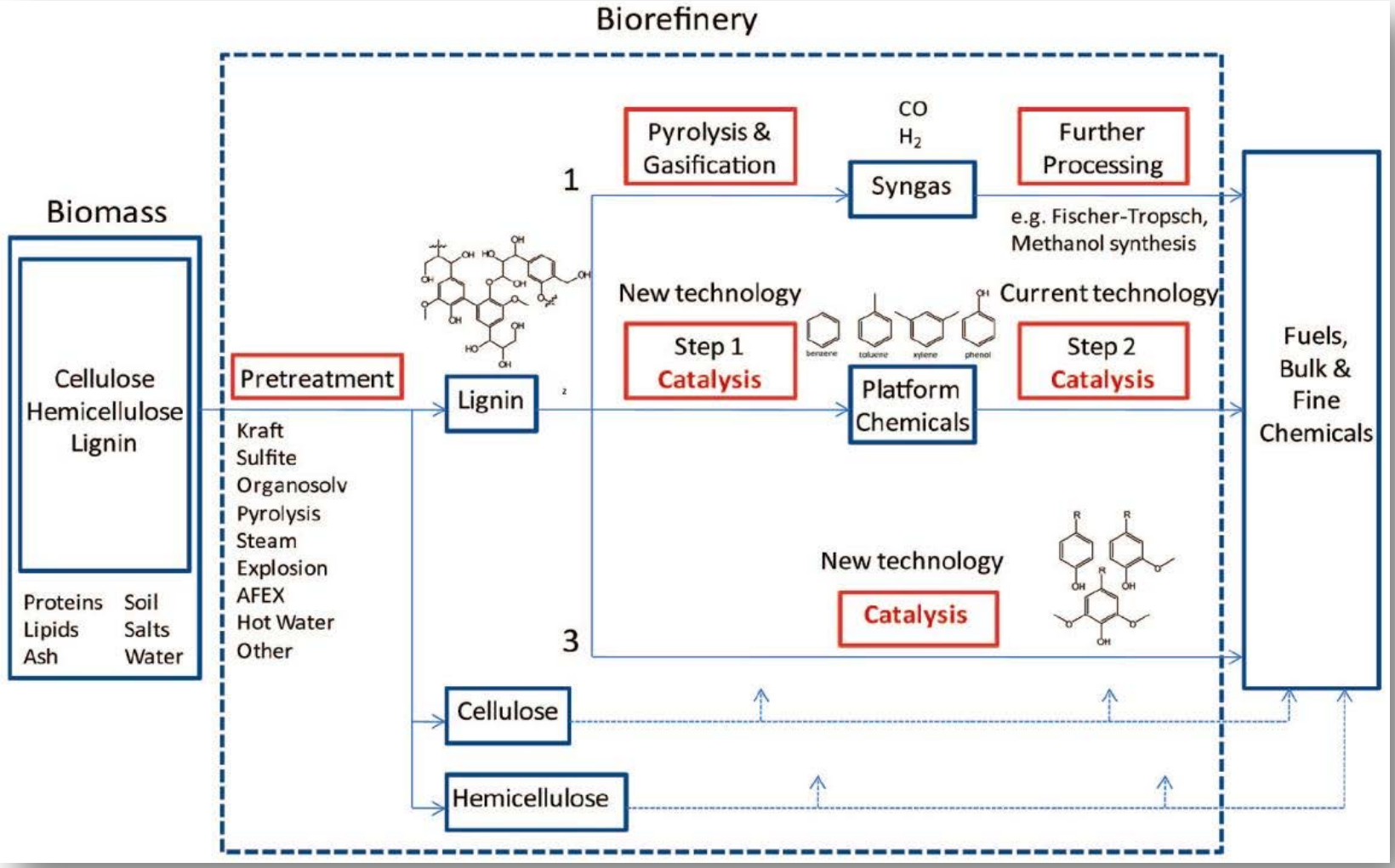
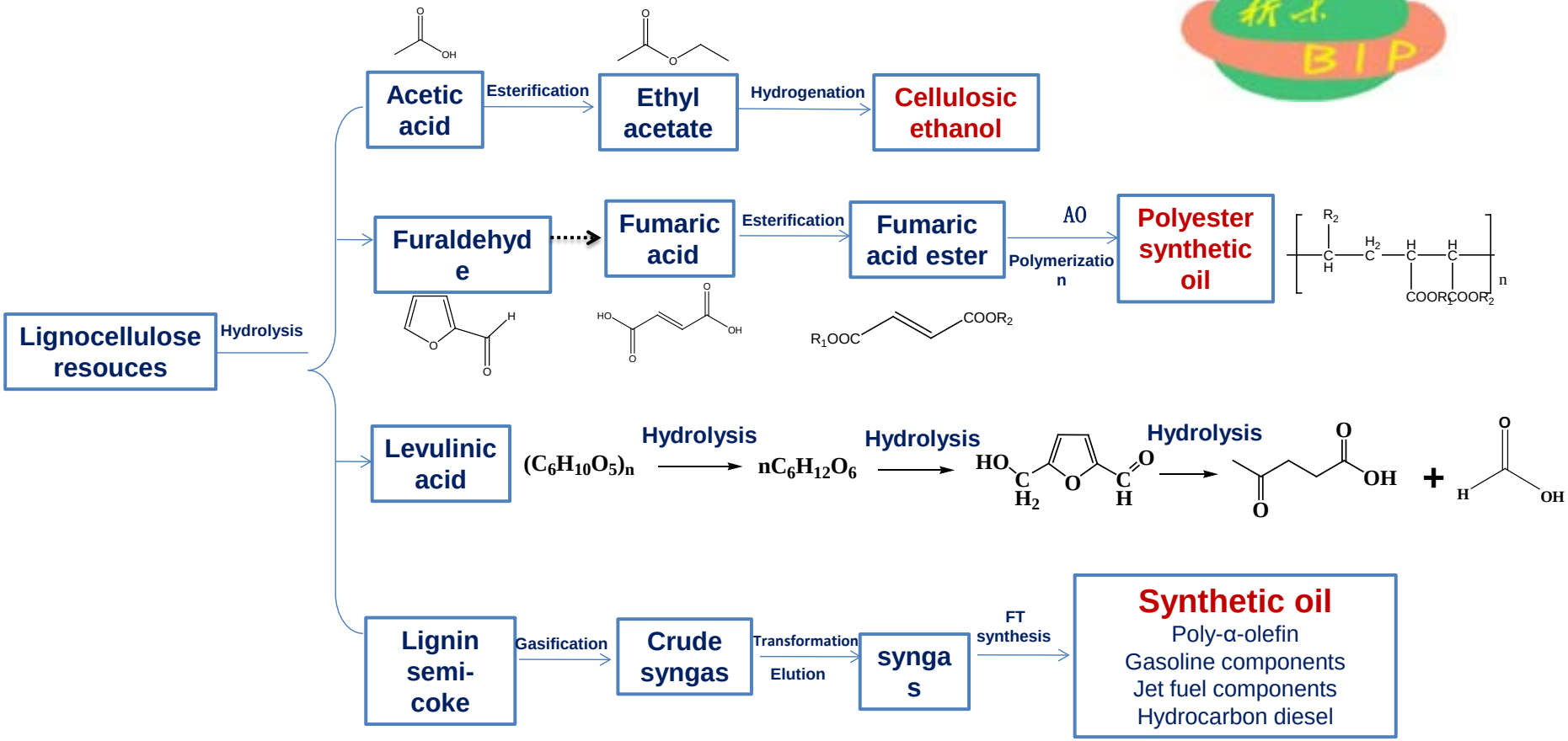
Lignocellulose application



Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, Bert M. Weckhuysen. Chem. Rev. 2010, 110, 3552–3599.

Lignocellulose application



Technology roadmap of lignocellulose resouces application, cooperated with Xinmu Corporation.

International Cooperation energy

Research Cooperation

Prof. Dr. Johannes A. Lercher
Technical University of Munich
& Pacific Northwest National Laboratory

Prof. Dr. Xuebing Li
QIBEBT, CAS

Prof. Dr. Martin Muhler
Ruhr-University Bochum

QIBEBT

Sino-German Project-2016

国家自然科学基金委员会
National Natural Science Foundation of China

Deutsche Forschungsgemeinschaft

Mesoporous Carbon Supported Metal Catalysts for Sustainable Hydrogenation Reactions

¥ 2.535 Million RMB

Financial Support

Research, Training, Exchange, Summer School… ?

Institute and group

Qingdao Institute of Bioenergy and Bioprocess Technology

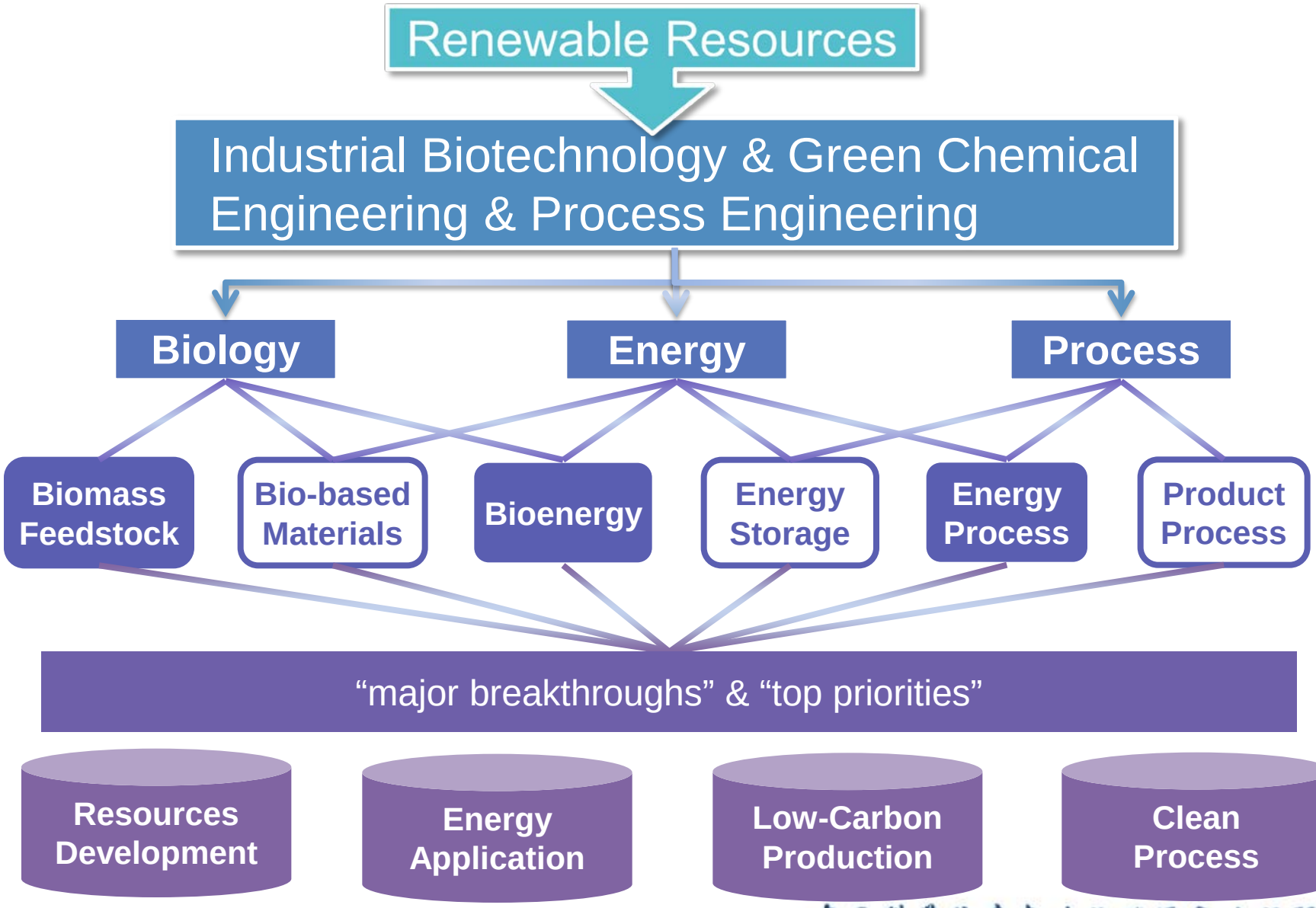
Qingdao Institute of Bioenergy and Bioprocess Technology

One of China's primary national research institutions for renewable energy and green materials, focusing mainly on R&D of the resources, technologies, products and processes for bio-based energy and materials.

Devoted to providing systematic and sustainable solutions to China's bioenergy needs by integrating science, technology, and engineering in the fields of industrial biology, green chemical technology, and process engineering.

- Co-found by CAS, Shandong and Qingdao
- Officially operated since 2007
- More than 400 research staff
- 180 Postgraduate students
- Unique capabilities
- Synergy innovation with government, industry and universities

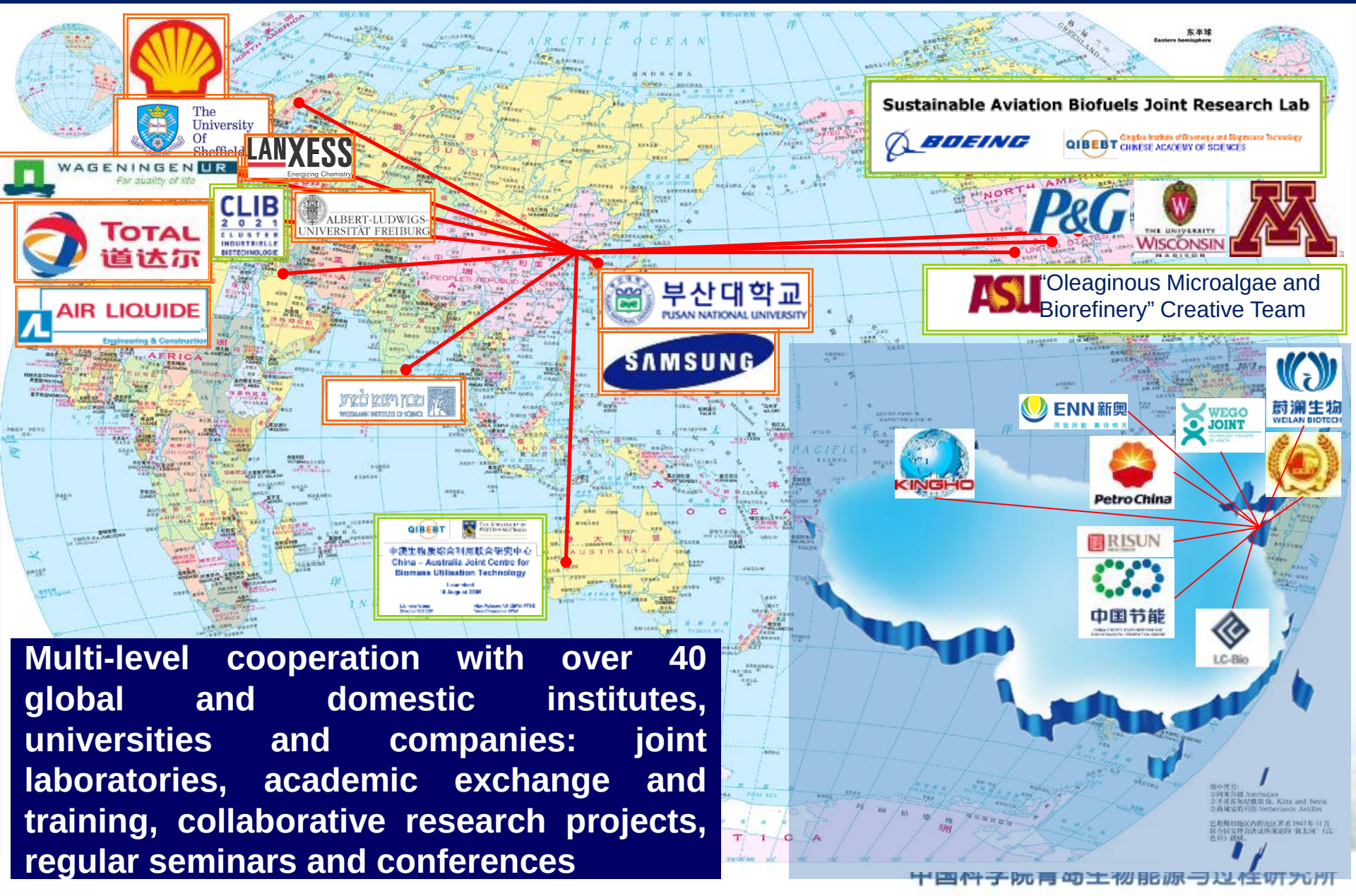
Qingdao Institute of Bioenergy and Bioprocess Technology



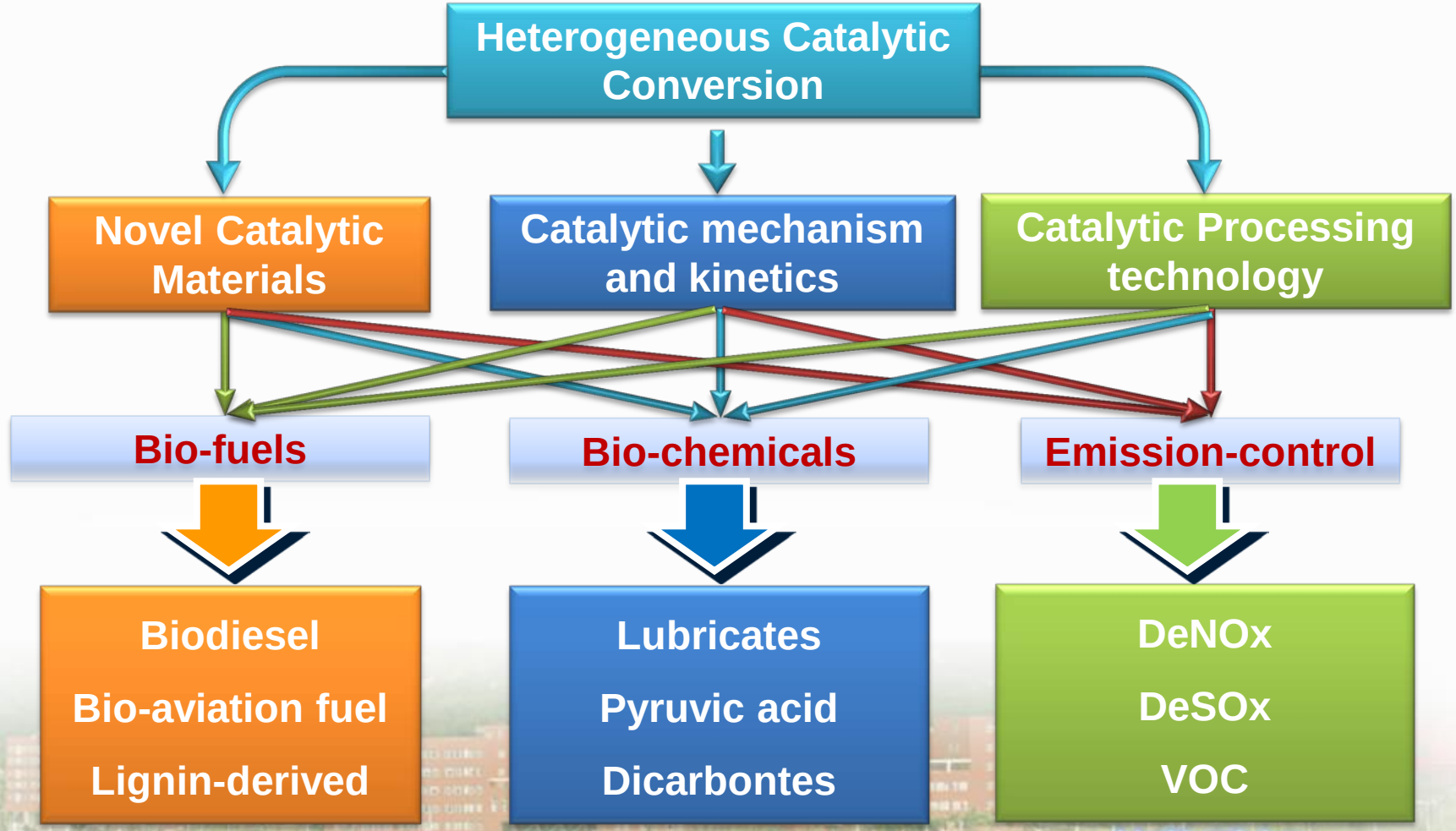
中国科学院青岛生物能源与过程研究所

Research and Academic Cooperation

---global partnership for excellence in green energy and materials for a sustainable Earth



Multi-level cooperation with over 40 global and domestic institutes, universities and companies: joint laboratories, academic exchange and training, collaborative research projects, regular seminars and conferences


Heterogeneous Catalytic Conversion
Novel Catalytic Materials
Catalytic mechanism and kinetics
Catalytic Processing technology
Bio-fuels
Bio-chemicals
Emission-control
Biodiesel
Bio-aviation fuel
Lignin-derived
Lubricates
Pyruvic acid
Dicarbontes
DeNOx
DeSOx
VOC

Comments & Questions

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