Extension of 'Solvent Treatment Method' Developed by SATREPS Program to ASEAN Region

2 February 2019

Nakorn Worasuwannarak

The Joint Graduate School of Energy and Environment
King Mongkut's University of Technology Thonburi

Japan-Thailand SATREPS Project

"Development of clean and efficient utilization of low rank coals and biomass by solvent treatment"

Kouichi Miura
Institute of Advanced Energy,
Kyoto University

Bundit Fungtammasan
JGSEE/King Mongkut's University of
Technology Thonburi

Cooperative Structure of our project

Japan

Head Investigator: Kouichi Miura
Research fund: 178 million yen from JST

Kyoto University: Miura Gr.
Kouichi Miura, Specially App. Prof.
Hideaki Ohgaki, Prof
Ryuichi Ashida, Assist. Prof.
Motoaki Kawase, Prof.
Taro Sonobe, Research Administrator
Janewit Wannapeera, Dr.
Trairat Muangthong-on, PhD cand.

Akita University: Sugawara Gr.
Katsuyasu Sugawara, Prof.
Takahiro, Kato, Assis. Prof.
Kenji Murakami, Prof.

CRIEPI: Makino Gr.
Hisao Makino, Dr.
Kenji Tanno, Dr.
Satoshi Umemoto, Dr.
Atsushi Ikeda, Mr.
Shiro Kajitani, Dr.

Kobe Steel Co. Ltd: Okuyama Gr
Noriyuki Okuyama, Dr.
Takuya Yoshida, Dr.
Shigeru Kinoshia, Mr.
Koji Sakai, Mr.

Thailand

Head Investigator: Bundit Fungtammasan
Research fund: 300 million yen from ODA

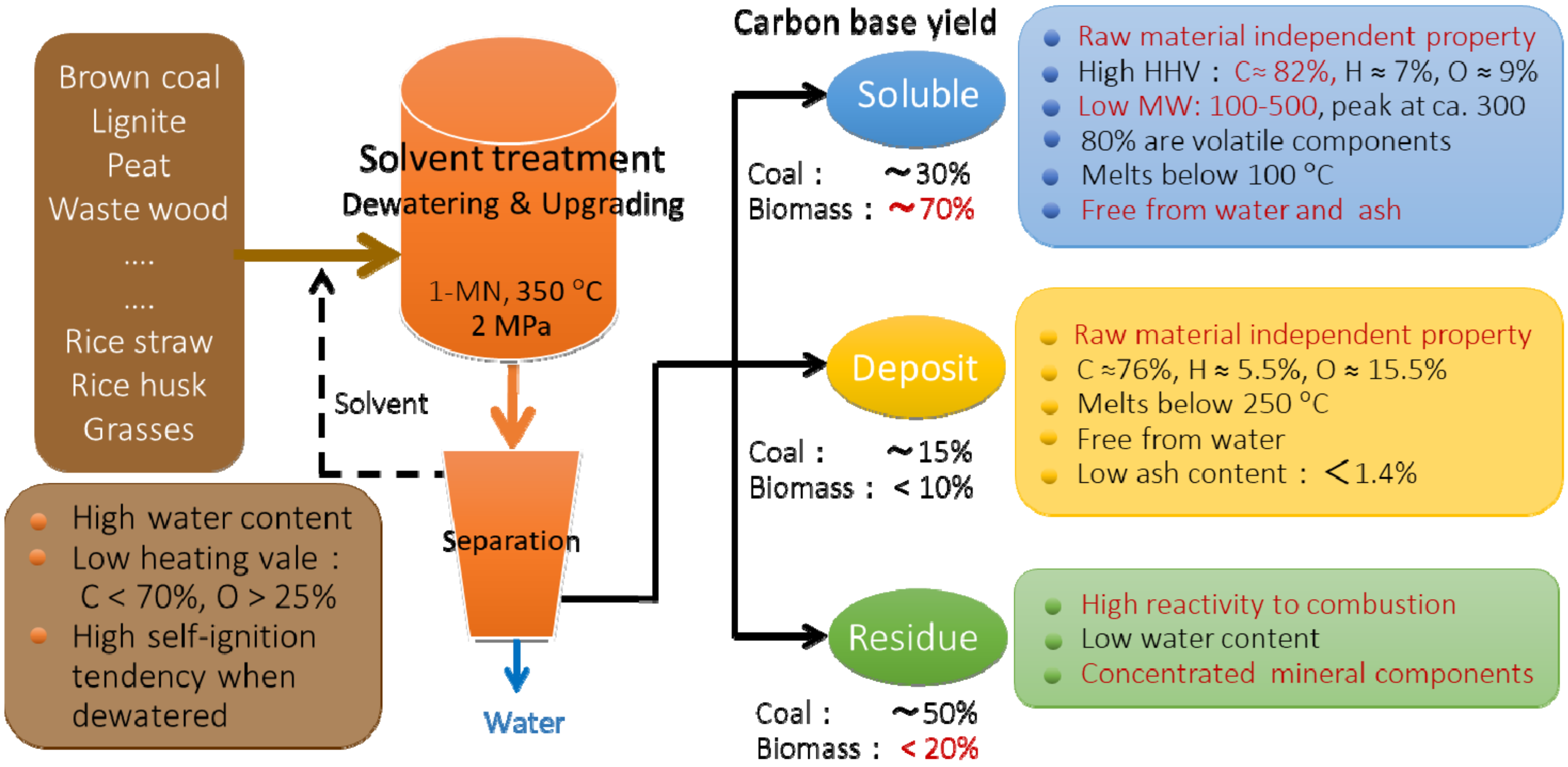
JGSEE/KMUTT: Bundit Gr.
Assoc.Prof. Bundit Fungtammasan
Assoc.Prof. Sirintornthep Tawprayoon
Assoc.Prof. Nakorn Worasuwannarak
Assoc.Prof. Suneerat Fukuda
Dr. Supachita Krerkkaiwan
Ms. Sasithorn Buranatrevedhya
Mr. Supachai Jadsadajerm
Mr.Jaggapan Sanduang
Ms.Thitima Sornpitak
Mr.Kaweewong Wongaiyara

PTT-RTI, PTT Public Company Ltd: Arunratt Gr.
Arunratt Wuttimongkolchai, Ms.
Suttipong Tunyapisetsak, Mr.
Suchada Butnark, Dr.
Anurak Winitsorn, Dr.
Suriya Porntangjitlikit, Mr.
Kornthape Prasirtsiripham, Mr.

Four research groups from Japan and two research groups from Thailand are involved in this project.

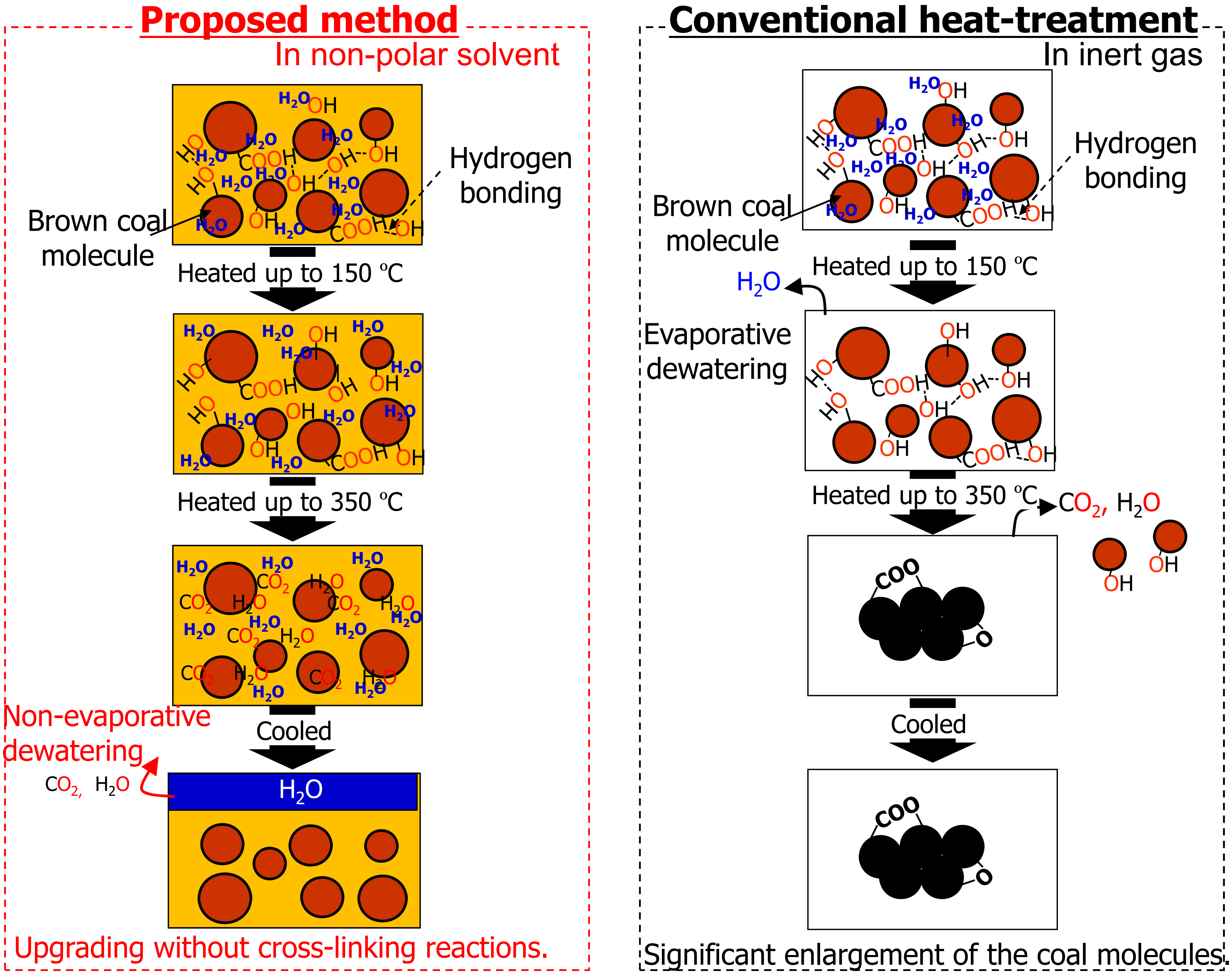
More than 30 researchers fro ny and industry contribute to

Concept of Solvent Treatment



The method dewaters and upgrades various low-grade carbonaceous resources, producing high quality extract in high yield under mild conditions.

- Almost no heating value loss through the treatment
- Soluble and Deposit have raw material independent properties


Proposed method
In non-polar solvent
Hydrogen bonding
Brown coal molecule
Heated up to 150 ℃
Heated up to 350 ℃
Non-evaporative dewatering
Cooled
CO_2, H_2O
H_2O
Upgrading without cross-linking reactions.
Conventional heat-treatment
In inert gas
Hydrogen bonding
Brown coal molecule
Heated up to 150 ℃
H_2O
Evaporative dewatering
Heated up to 350 ℃
CO_2, H_2O
Cooled
Significant enlargement of the coal molecules.

METHODOLOGY

Reaction conditions **(20 g : 400 ml)**
Temperature: **350 °C**
Reaction time: **60 min**
Media: **Kerosene, A150 and 1-MN**

The extracted product which was recovered as solid by removing solvent

Soluble

Liquid

The small molecules which removed by the rotary evaporator with the solvent

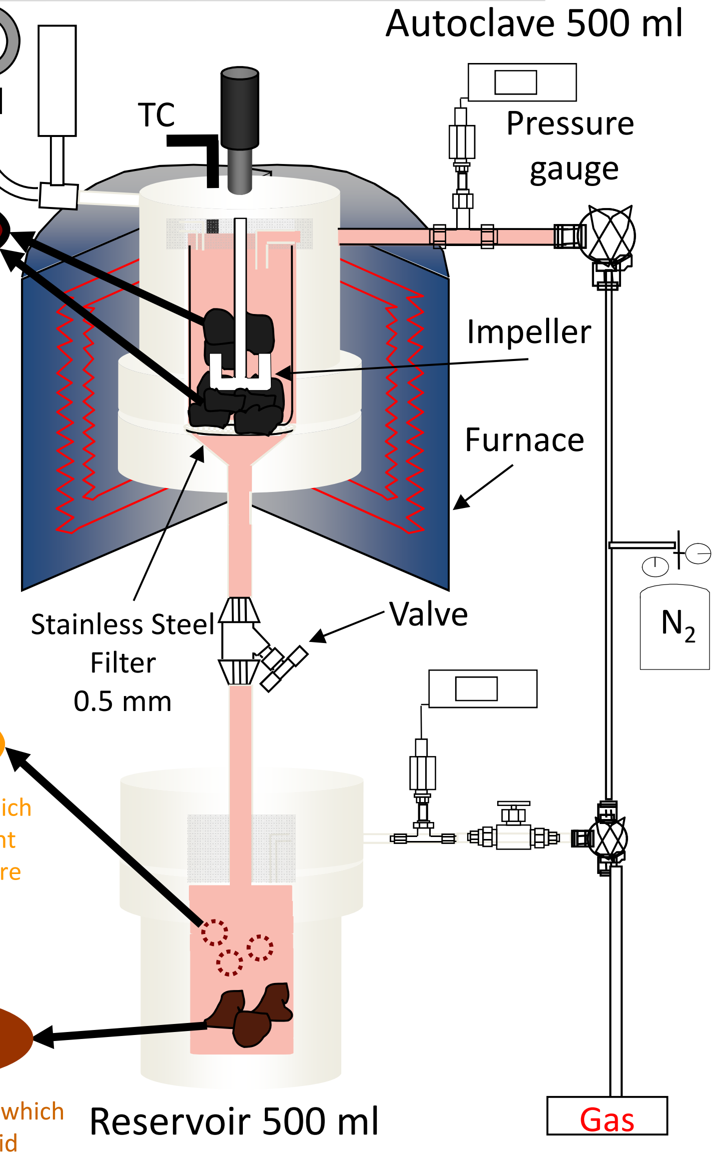
Sample

Extracts

The extracted fraction which was soluble in the solvent even at room temperature

Deposit

The extracted fraction which precipitated as solid at room temperature



Gas

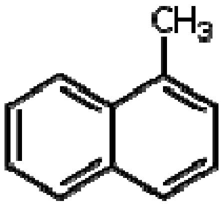
Raw materials used

Brown coal (Loy Yang)

Rice straw

Leucaena

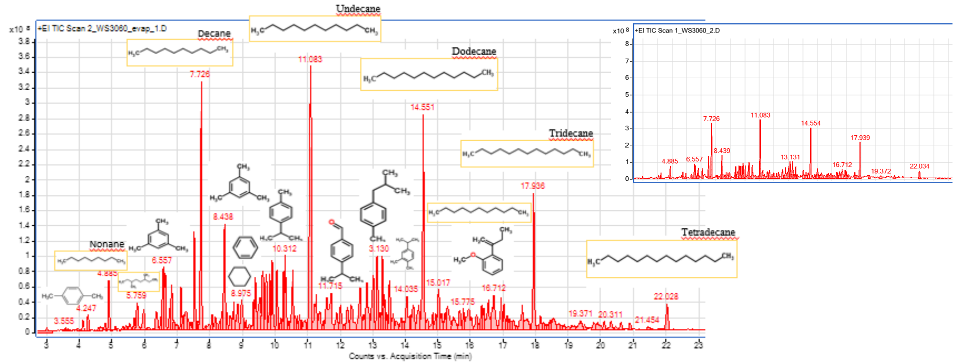
Solvents used



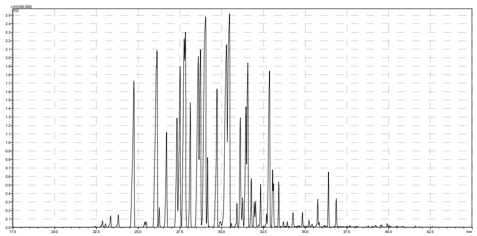
1-Methylnaphthalene (1-MN)

- Non polar
- Non hydrogen donor

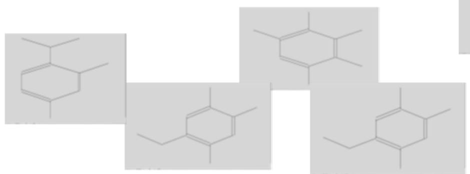
Kerosene (WS3060)

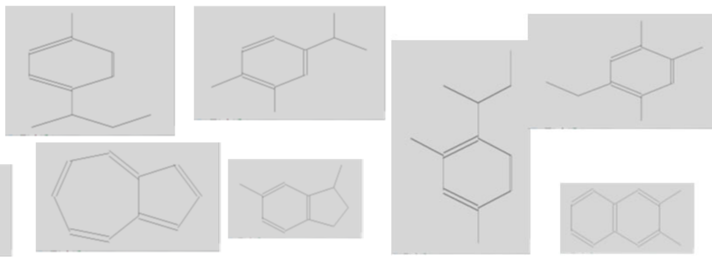


A 150

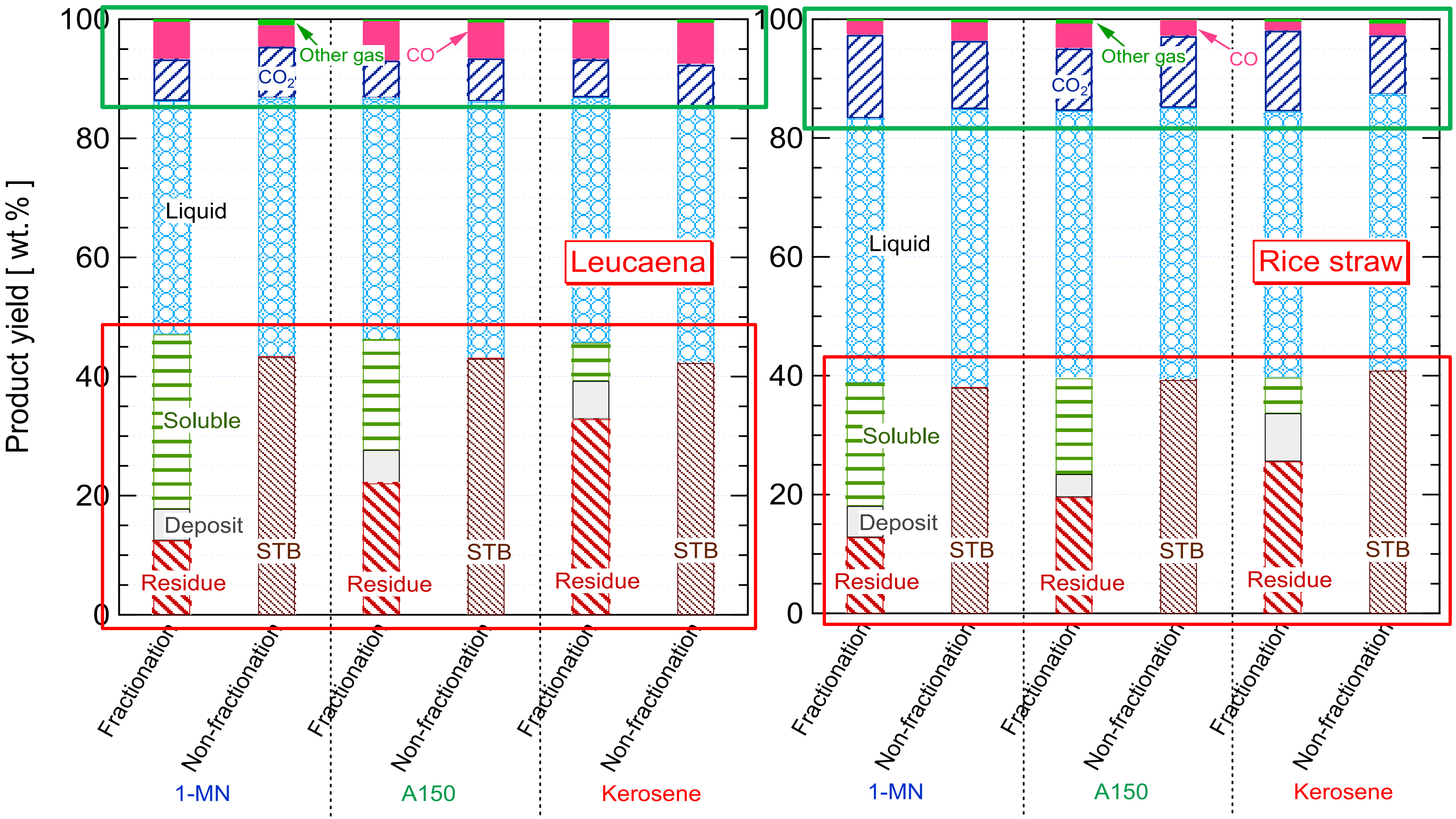


Benzene derivative





Product distributions using different solvents



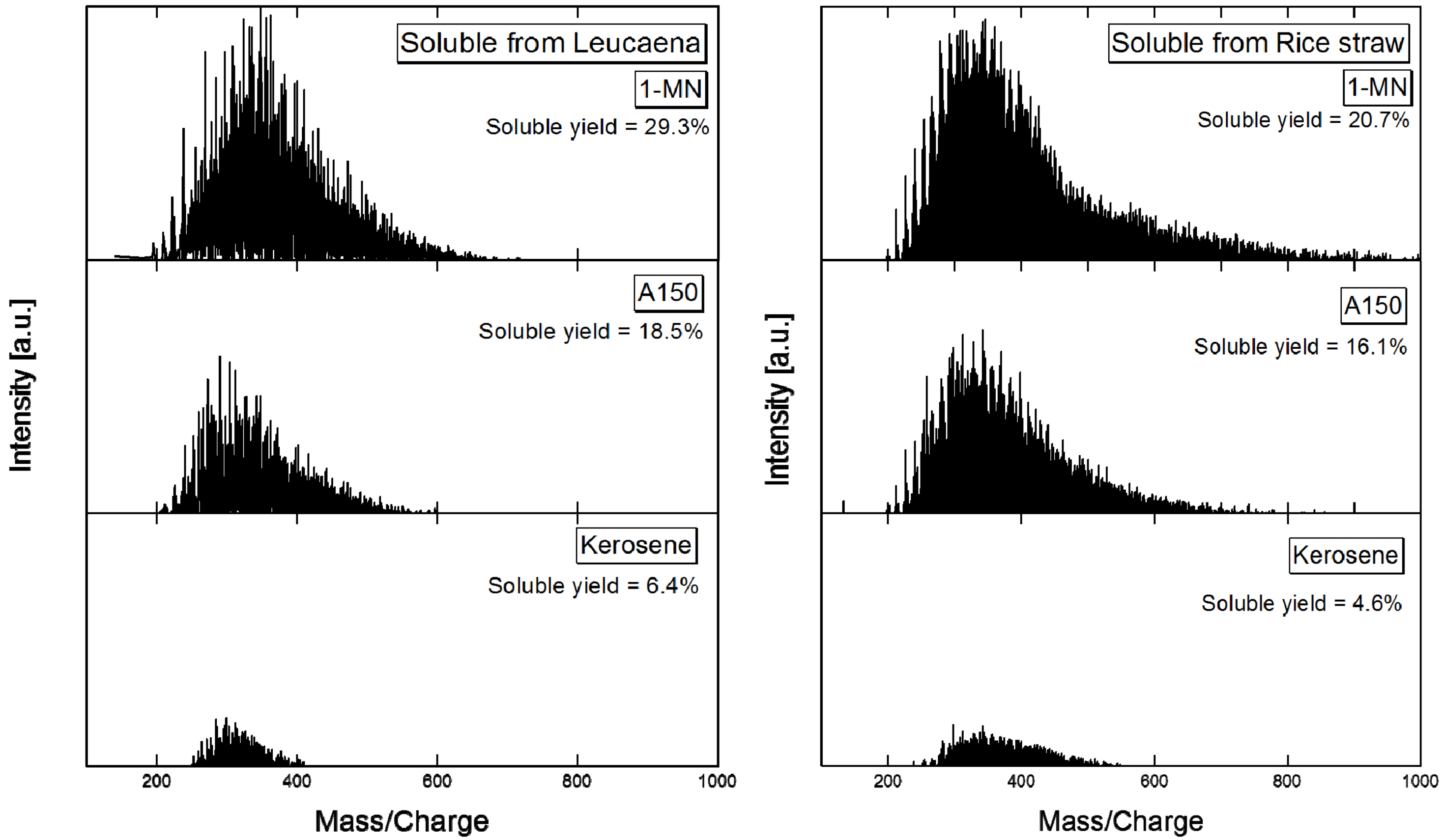
- The solvent did not affect the degradative reaction at 350°C.
- The solvent affected significantly the distribution of extracts.
- The difference in distribution of the extracts can be well explained by the difference in the solubility of the solvents.

Analyses of Solubles and Upgraded products

Sample	Yield [wt %, d.a.f.]	Ultimate analysis [wt %, d.a.f.[a]]				Proximate analysis [wt %, d.b.[b]]			Atomic ratio [-]		HHV [MJ/kg, d.a.f.]
		C	H	N	O (diff.)	VM	FC	ash	O/C	H/C	
Rice straw (RS)		42.5	6.5	0.6	50.4	72.2	13.6	14.2	1.84	0.89	14.7
Extraction in 1-MN											
Residue	12.8	61.3	4.8	1.0	32.8	32.9	14.9	52.3	0.95	0.40	21.7
Deposit	5.3	79.3	5.6	1.6	13.6	39.5	60.0	0.5	0.85	0.13	32.4
Soluble	20.7	84.7	7.1	1.0	7.1	66.9	33.1	0.0	1.01	0.06	37.6
STB	38.0	76.2	5.9	1.0	16.9	34.0	34.7	31.3	0.93	0.17	31.2
Extraction in Kerosene											
Residue	25.6	70.1	5.2	1.0	23.8	36.5	26.4	37.1	0.88	0.25	26.9
Deposit	8.1	81.3	6.7	1.8	10.2	60.8	39.2	0.0	1.00	0.09	35.3
Soluble	6.0	82.1	8.8	0.9	8.2	88.6	11.4	0.0	1.29	0.07	39.0
STB	40.9	72.3	6.0	0.9	20.8	30.8	35.0	34.2	1.00	0.22	29.3
Extraction in A150											
Residue	19.6	67.7	5.4	0.9	26.0	30.4	35.0	34.6	0.95	0.29	26.0
Deposit	3.9	80.4	6.0	1.7	11.8	45.3	54.7	0.0	0.90	0.11	33.7
Soluble	16.1	80.8	7.7	1.2	10.3	75.1	24.9	0.0	1.14	0.1	36.6
STB	39.3	75.4	6.3	0.9	17.4	34.1	33.7	32.2	1.00	0.17	31.4

Soluble prepared by different solvents have similar properties

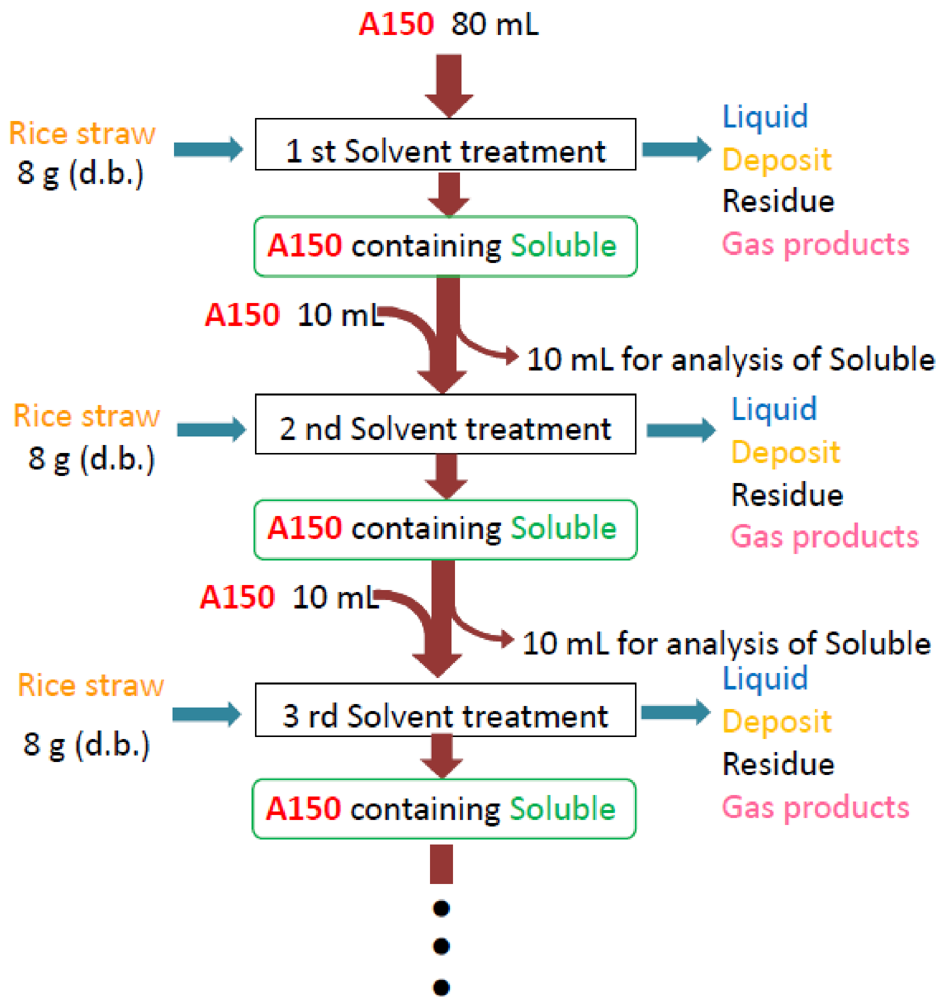
MWD of Solubles prepared from various solvents



- To compare the MWD quantitatively, the intensity is multiplied by the yield of Solubles.
- MWD of Solubles are similar and do not depend on the solvent.

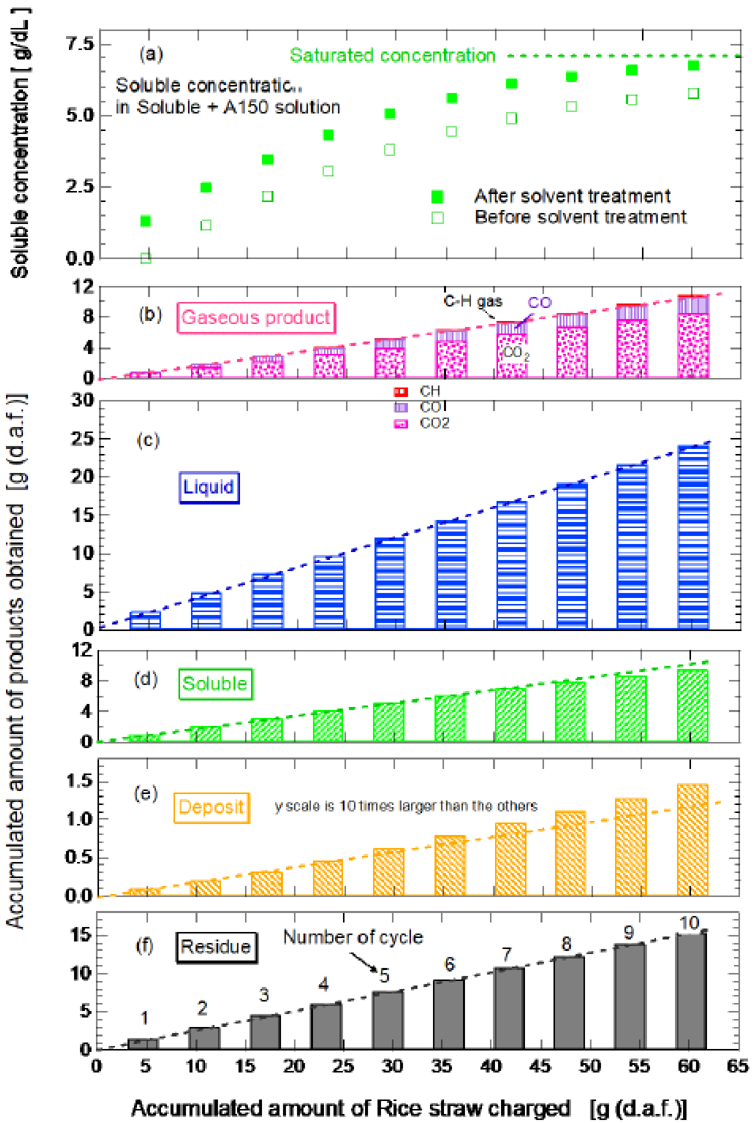
A150 could be successfully selected as a practical solvent!

Development of effective extraction scheme to minimize solvent to coal/biomass ratio



Solvent-Soluble mixture is used repeatedly by replacing around 10 % by fresh A150

Development of effective extraction scheme to minimize solvent to coal/biomass ratio



- Repeated use of Solvent-Soluble mixture little affects the product distribution
- Soluble is almost saturated in product mixture of Solvent-Soluble

Conventional (One batch operation)

Rice straw to A150 ratio = **1/10**

5-Step operation

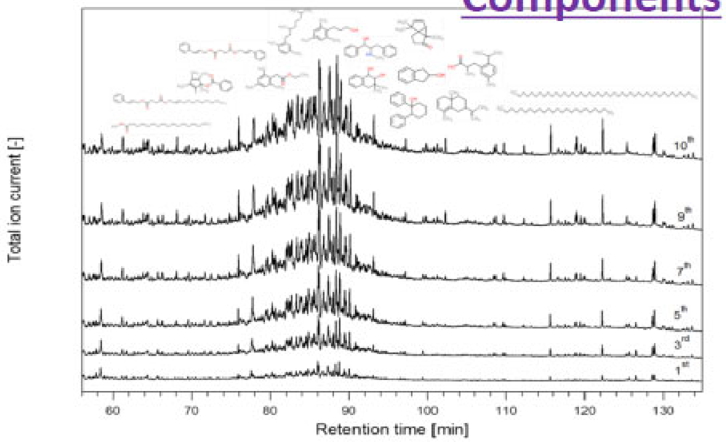
Rice straw to A150 ratio = **1/3**

10-Step operation

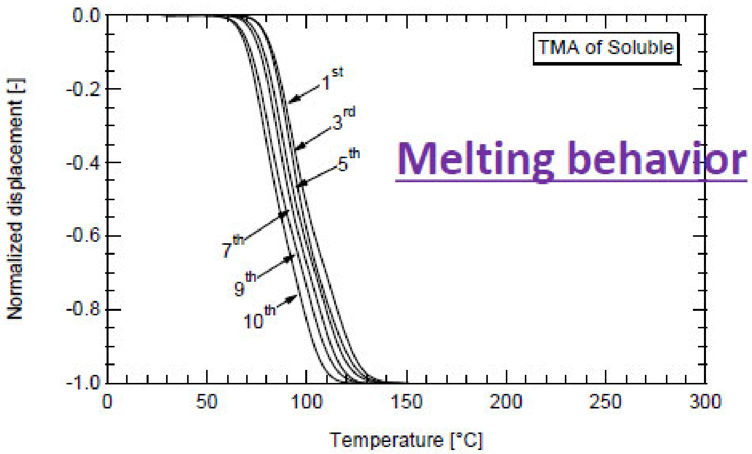
Rice straw to A150 ratio = **1/2.1**

Effect of repeated use of Solvent-Soluble mixture on Soluble properties

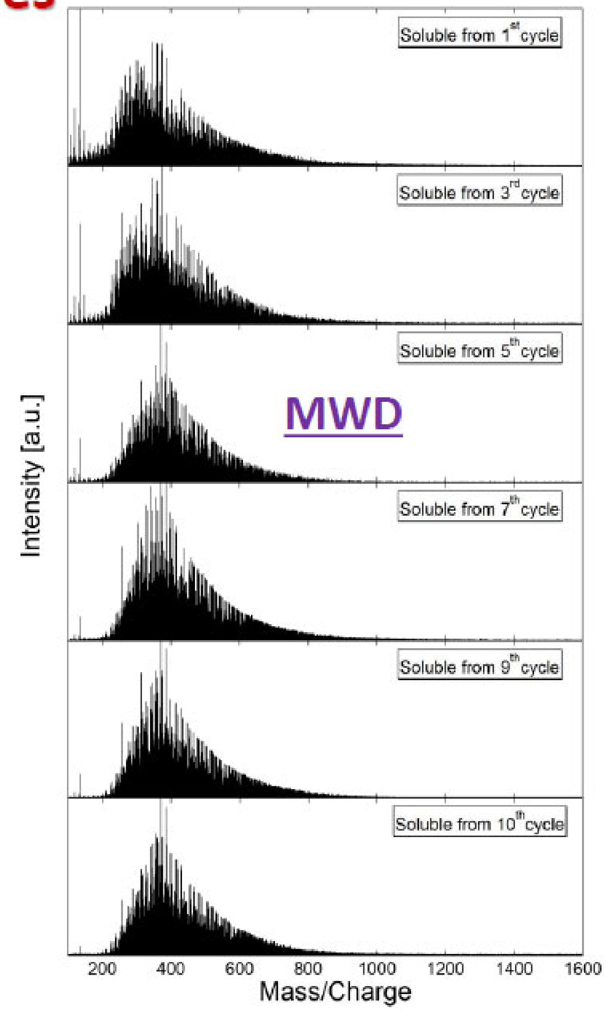
Components



Melting behavior

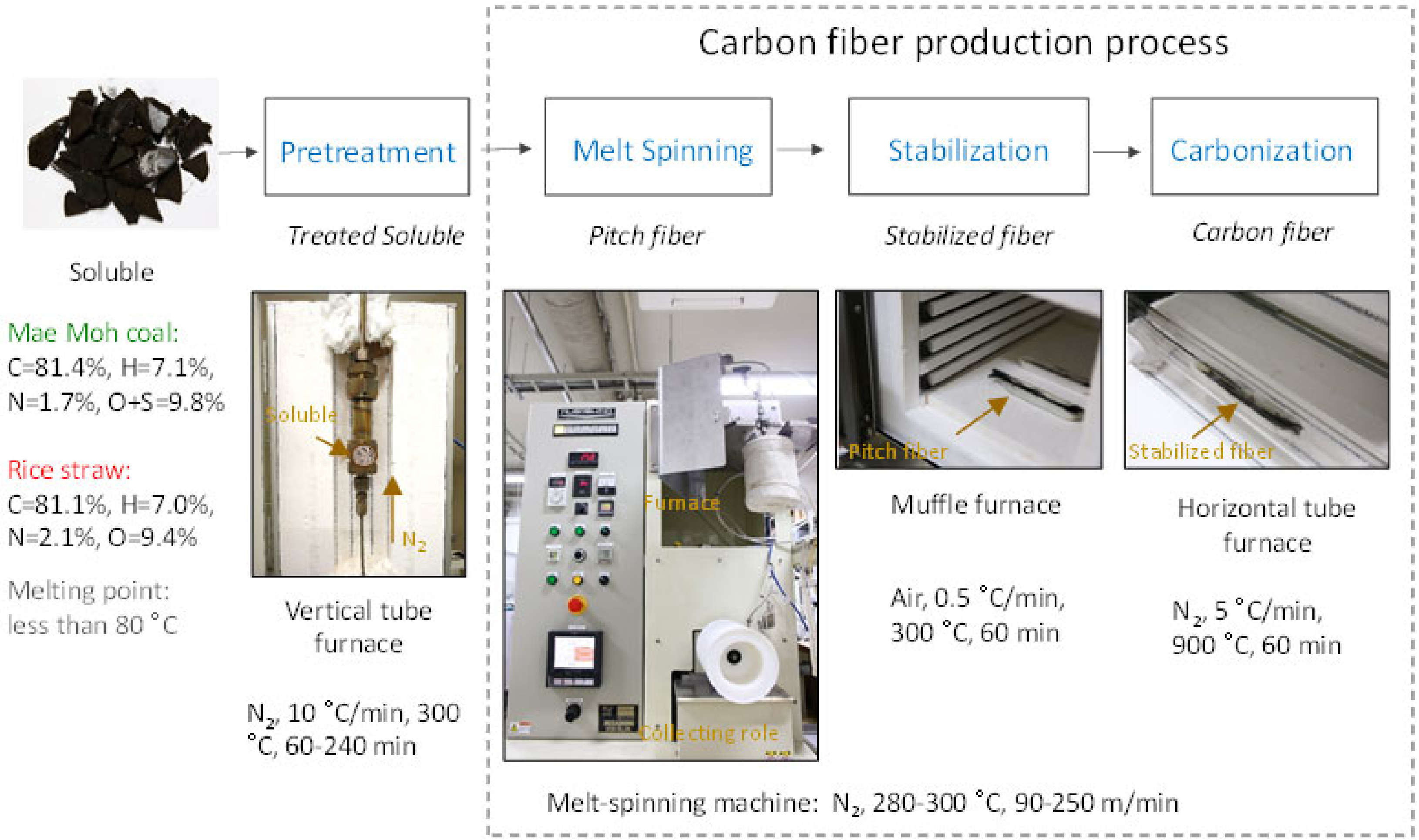


MWD

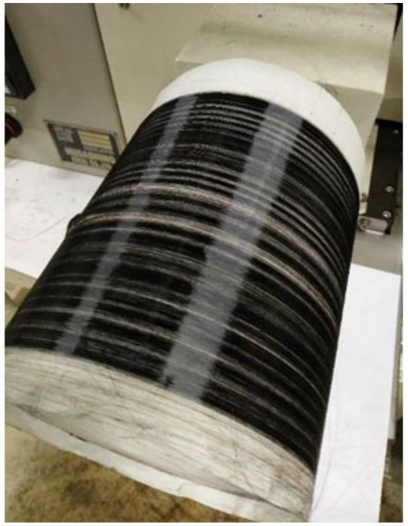


Soluble properties are little affected by the repeated use of Solvent-Soluble mixture

Production of carbon fiber from Solubles

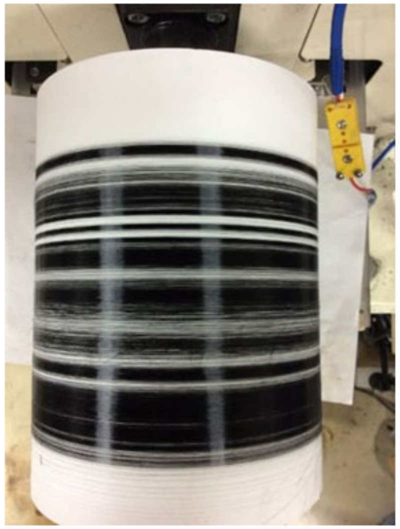


Appearance of carbon fibers



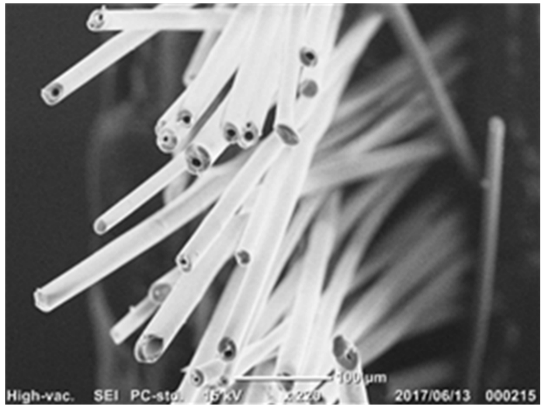
RS(300 °C-80min)

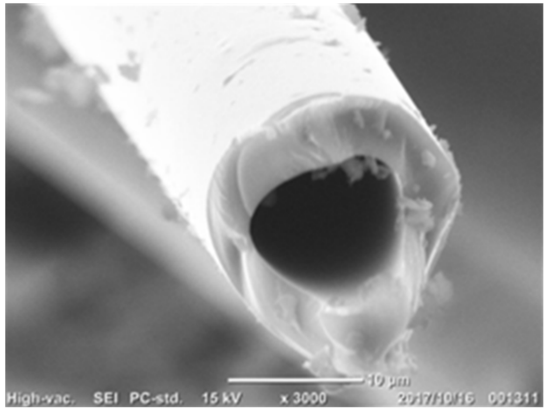
MM coal (300 °C-100min)

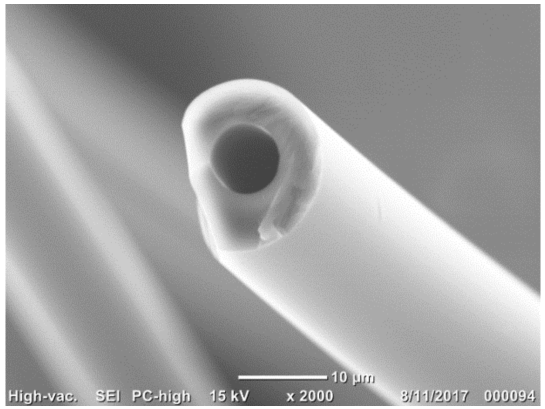


PTT coal （C_6H_{12} ext. + 240 °C-120min）

RS by A150 (320 °C-120min)







Tensile strength of carbon fibers

表 3-2　調製した炭素繊維の平均径と強度

Carbon fiber (CF)	Average diameter [μm]	Tensile strength [MPa]	Elastic tensile modulus [GPa]
RS Soluble			
CF280°C-60 min	9 ± 2	79 ± 36	-
CF300°C-80 min	20 ± 3	148 ± 36	29 ± 8
CF300°C-100 min	24 ± 4	378 ± 85	48 ± 19
MM coal Soluble			
CF300°C-100 min	12 ± 0.8	275 ± 53	52 ± 25
CF300°C-180 min	17 ± 0.6	285 ± 46	-
CF300°C-240 min	20 ± 2.0	300 ± 50	43 ± 25
RS Soluble (A150)			
CF320°C-120 min	21 ± 2.0	376 ± 90	-

Production of activated carbon fibers (ACFs)

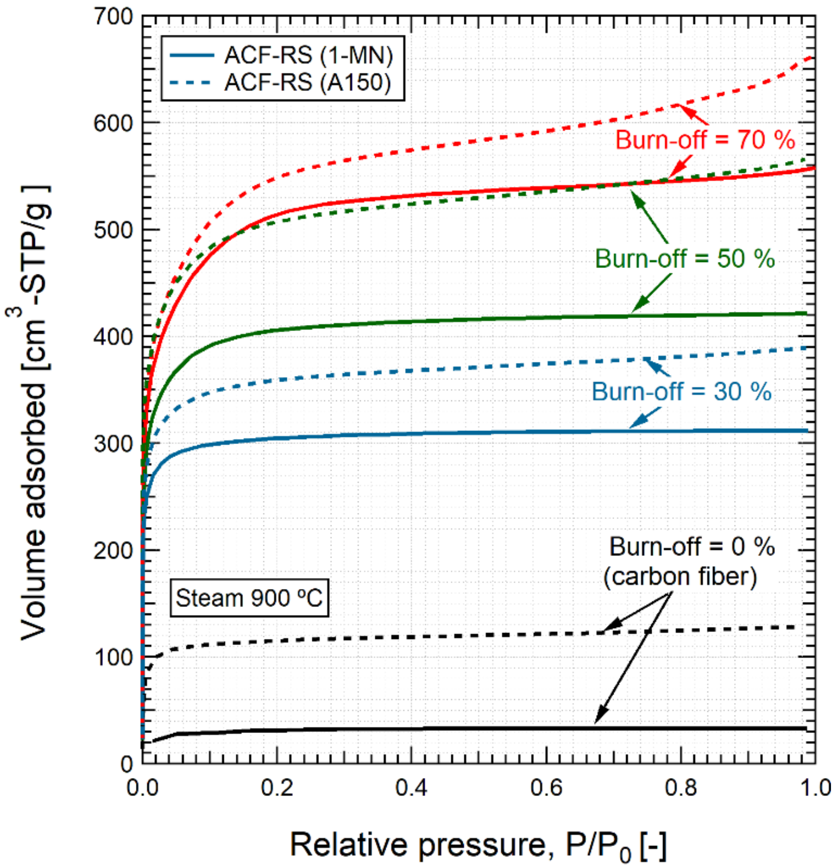
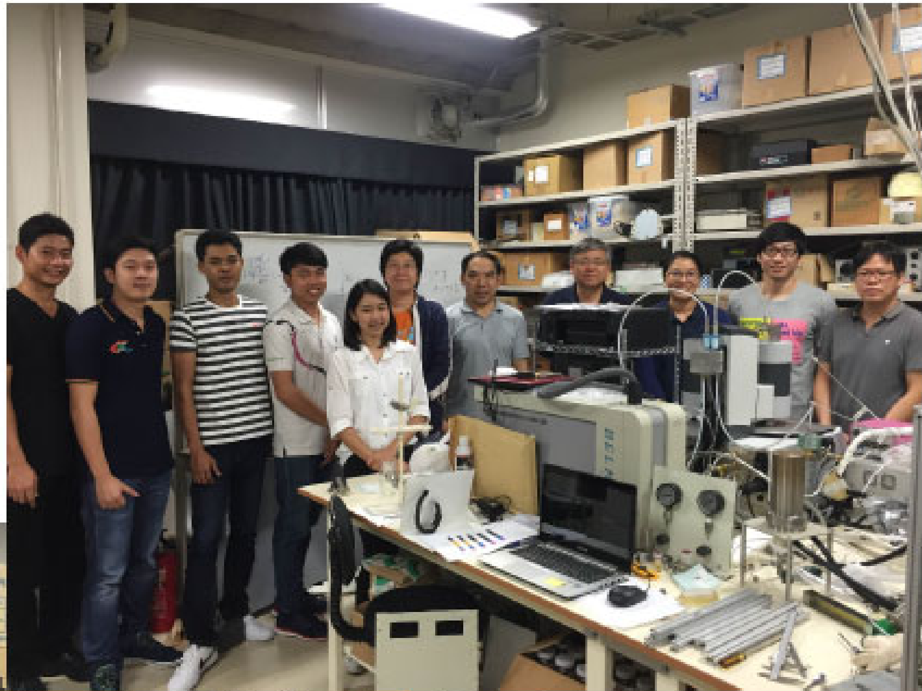
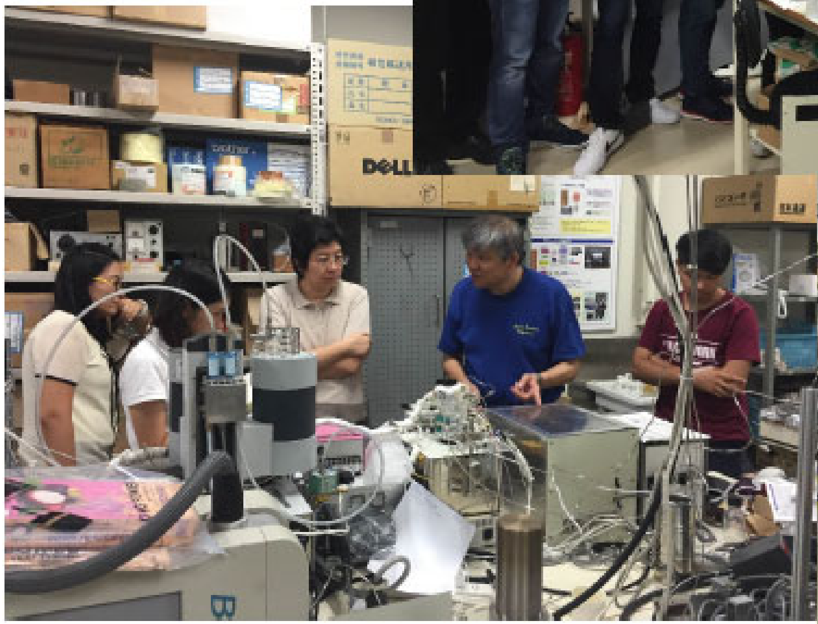


表 3-3 炭素繊維を水蒸気賦活して得られた活性炭素繊維の細孔特性

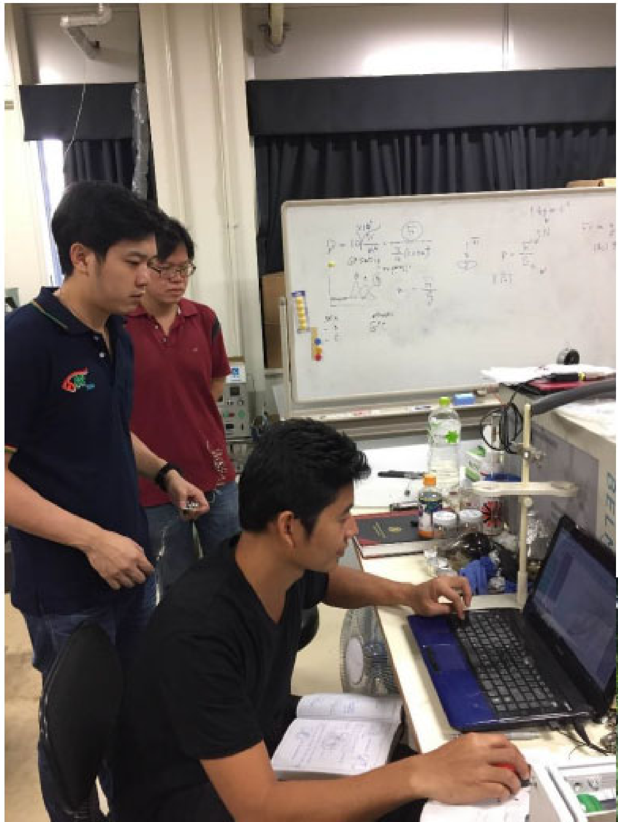
Sample	Burn-off [%]	S_{BET} [m²/g]	Accumulated pore volume [cm³/g]	Average pore diameter [nm]
Prepared from the Soluble obtained by 1-MN extraction of RS				
CF (Non-activated)	0	114	0.05	1.79
ACF (850 °C activation)	30	1149	0.47	1.63
	50	1540	0.66	1.71
	70	1882	0.87	1.84
ACF (900 °C activation)	30	1181	0.48	1.63
	50	1529	0.65	1.71
	70	1865	0.86	1.85
Prepared from the Soluble obtained by A150 extraction of RS				
CF (Non-activated)	0	387		
ACF (900 °C activation)	30	1326	0.60	1.81
	50	1854	0.87	1.89
	70	1966	1.02	2.08

Training at Kyoto University Sep. – Oct., 2016





Training at Kyoto University   Sep. – Oct., 2016



Training at Kyoto University, Sep – Oct 2018

Output

- International journal: 3 papers
- International conference: 14 papers
- 4 Master students
- 1 Ph.D. student

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Effect of Solvent on the Degradative Solvent Extraction of Low Rank Coal

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Solvent Recycling Operation of the Degradative Solvent Extraction of Biomass to Minimize the Amount of Solvent Required

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ABSTRACT: The authors have recently presented a degradative solvent extraction method to dewater, upgrade, and convert biomass wastes into three solid fractions which we call Soluble, Deposit, and Residue. The carbon based yield of Soluble, which is the smallest molecular weight fraction, reached as high as 70% for some biomass wastes. Solubles were free from water and mineral matters, and their physical and chemical properties were almost independent of raw materials. Soluble is expected to be utilized for preparing functional carbon materials such as carbon fiber, and hence, it is requested to maximize the Soluble yield with minimum energy requirement from a practical viewpoint. Since the largest energy consumption of this extraction method comes from the separation of Soluble from solvent, it is essential to minimize the solvent to Soluble ratio before separating Soluble from the solvent. On the other hand, a large solvent to biomass ratio is required to disperse the biomass in the solvent during the solvent treatment at around 350 °C. To compromise the conflicting demands and to minimize the solvent to Soluble ratio, a new operating scheme, which uses the Soluble−solvent mixture repeatedly before separating Soluble from the solvent by replacing around 10% of the mixture by fresh solvent on every solvent treatment, was proposed. The validity of this operating scheme was examined by treating Thai rice straw (RS) with a general-purpose petroleum based solvent called A150 through 10 repeated uses of the Soluble−A150 mixture. It was found that the new operation scheme was effective from the viewpoints of quality and the yield of the Soluble produced.

1. INTRODUCTION

Biomass is an important renewable resource that has recently received growing attention. It is one of most abundant and

distillate rich in benzene derivatives (abbreviated to A150) could successfully be used to meet this requirement. Moreover, A150 could be separated easily from the extract product

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Degradative solvent extraction of biomass using petroleum based solvents

Supachai Jadsadajerm[a], Trairat Muangthong-on[b], Janewit Wannapeera[a,b], Hideaki Ohgaki[b], Kouichi Miura[b], Nakorn Worasuwannarak[a,*]
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Biomass
Solvent treated biomass
Kerosene

ABSTRACT

The aim of this study was to examine the possibility to use two petroleum based solvents, kerosene and distillate rich in benzene (A150), as practical solvents for the degradative solvent extraction at 350 °C in re ference to 1-MN. It was found that the thermal degradation behavior of two biomass samples, a rice straw an Leucaena, in the three solvents was rather similar and that only the distribution of Soluble, Deposit, and Residu was affected by the difference of solubility of the solvents. Preparation of solvent treated biomass (STB) using th three solvents gave the yields close to the sum of the yields of Soluble, Deposit, and Residue. It was judged tha A150 may be used to preparing Soluble and that Kerosene can well be used to prepare STB.

Expected Outcome/Future of our Project

- Implementation of a new technology for utilizing low rank coals and biomass wastes in Thailand.
- JGSEE/KMUTT and PTT-RTI help dissimilation of the technologies developed to ASEAN countries
- JGSEE/KMUTT works as a center of biomass conversion technology development and human resource building in ASAEN countries

Japanese members will assist such activities through JASTIP (Japan ASEAN Science and Technology Innovation Platform) program .

Thank you for your attention.