『亜臨界水・超臨界水中でのバイオマス変換』

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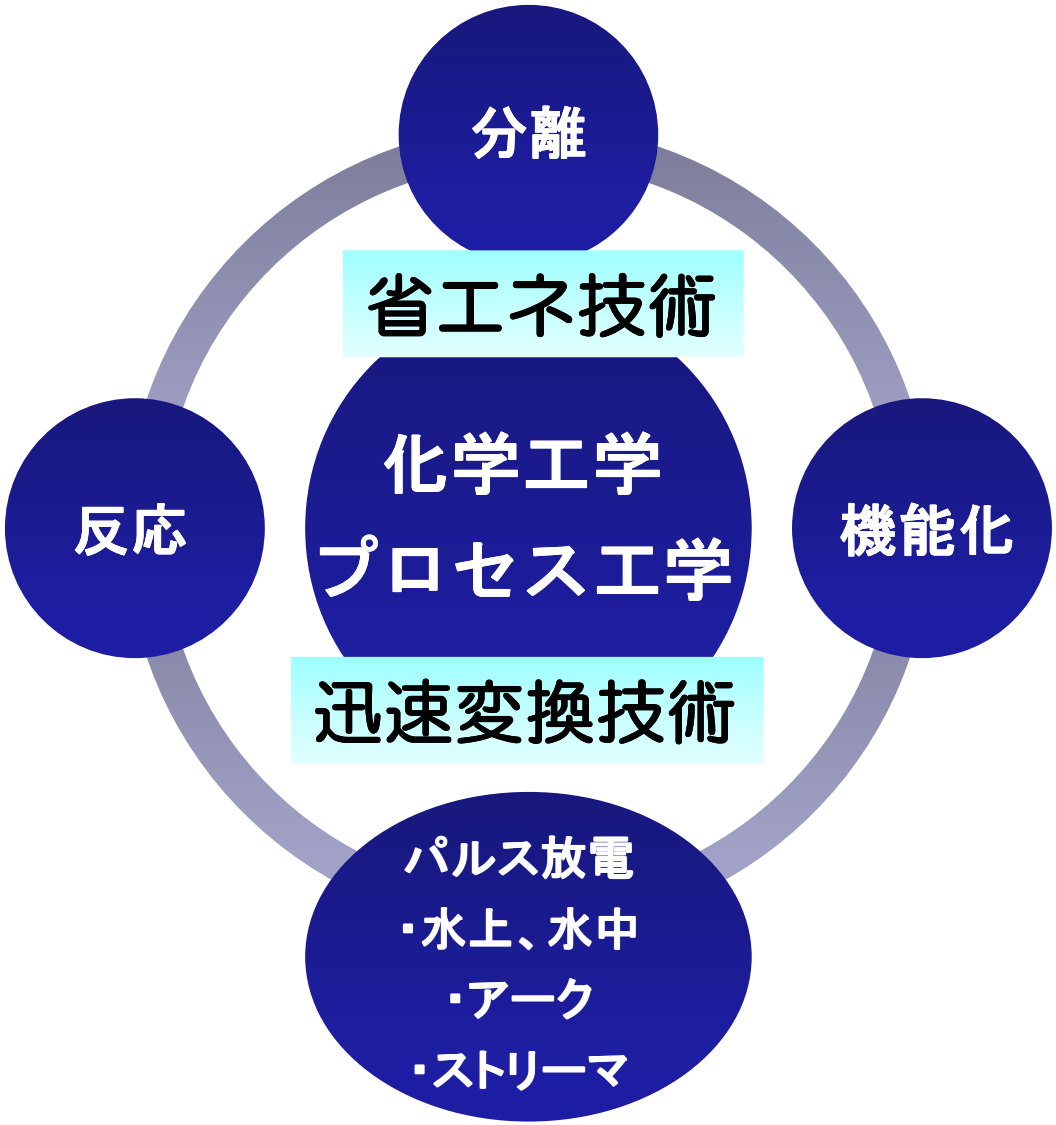
超臨界・亜臨界流体およびパルス放電を利用する技術による未利用・廃棄資源の再資源化



未利用バイオマスの有効活用

大型藻類からの有用成分抽出、炭素素材の作製

有機・無機複合材料の作製
例. AgNPs/PNIPAM、AgNPs/Fibroin等

食品加工残渣の有効活用

超臨界・亜臨界流体による機能性成分の抽出

バイオマス由来の機能性素材への変換

プラ・複合材料の化学リサイクル

水質汚染物質の分解・無害化

亜臨界水・超臨界二酸化炭素とは？

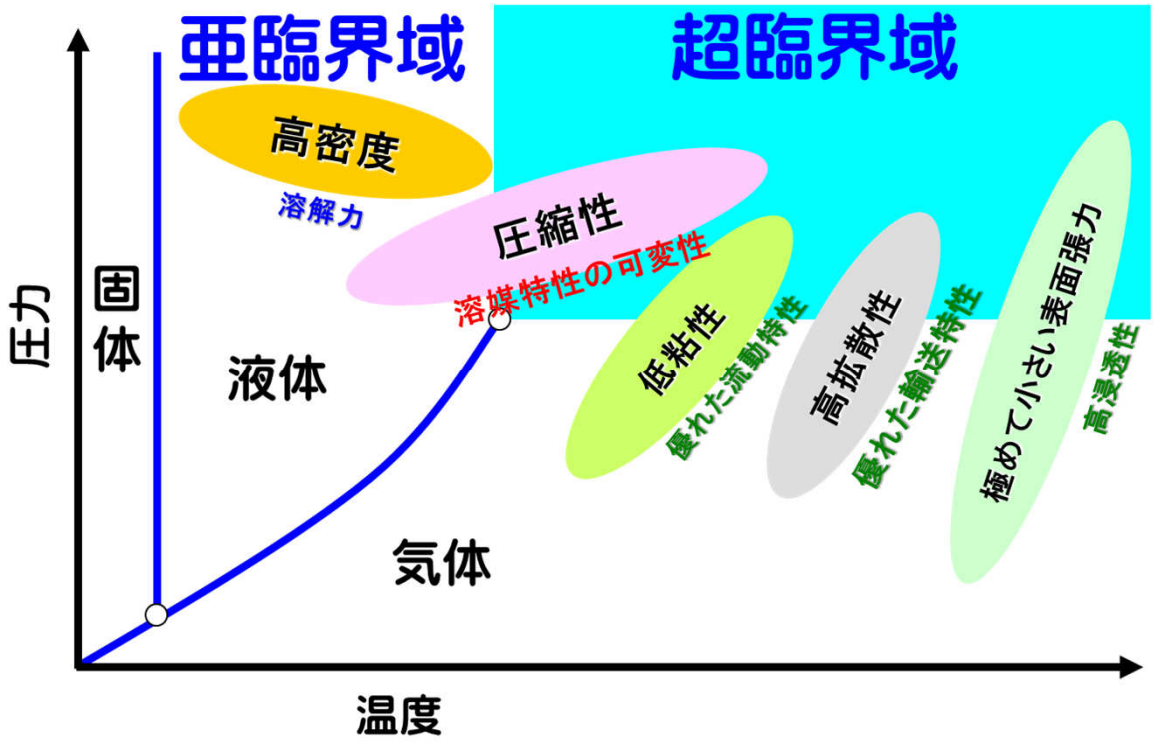


表. H_2OとCO_2の臨界定数

物質	臨界温度 [°C]	臨界圧力 [MPa]
H_2O	374.2	22.1
CO_2	31.1	7.4

亜臨界水

○高いイオン解離性
○高い加水分解速度
○高い極性物質の溶解性

超臨界二酸化炭素

○高い拡散性、表面張力ゼロ
○優れた低極性物質の溶解性
○無毒・無害、分離工程が簡便化

超臨界水・亜臨界水とは？

亜臨界水

◎ イオン積K_Wが高い

$H_2O \rightleftarrows H^+ + OH^-$

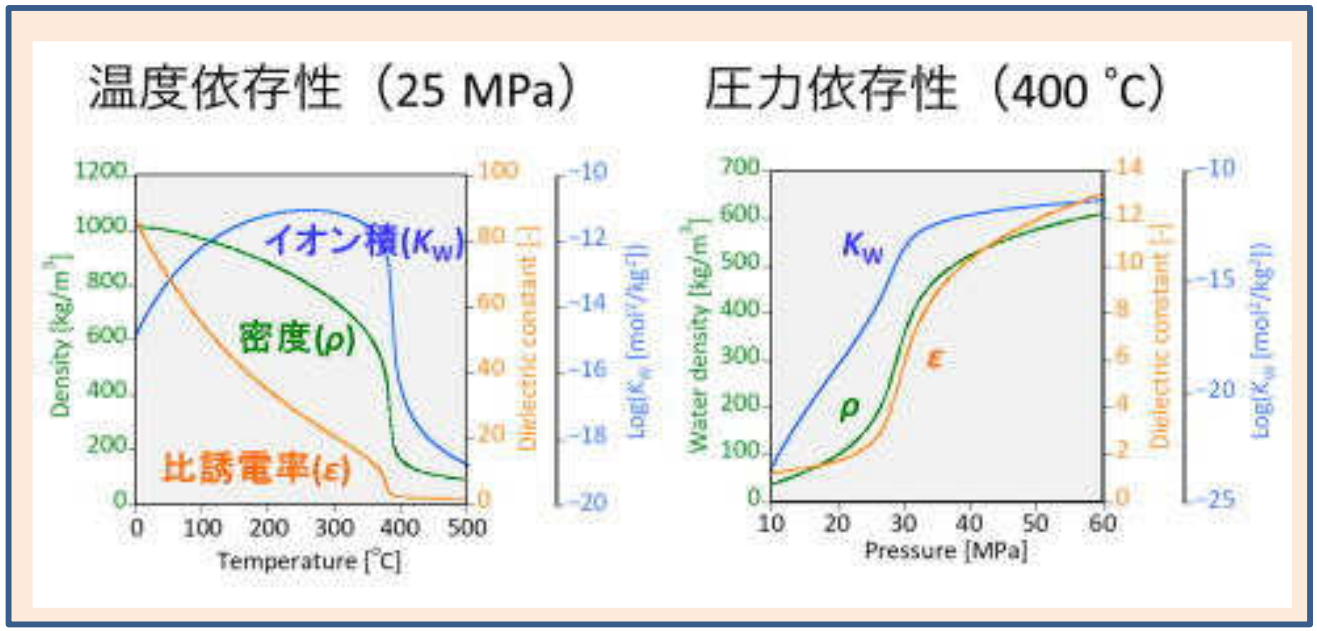
常温常圧の水 10^{-14} → 100~1000倍 → 亜臨界水 10^{-12}～10^{-11}

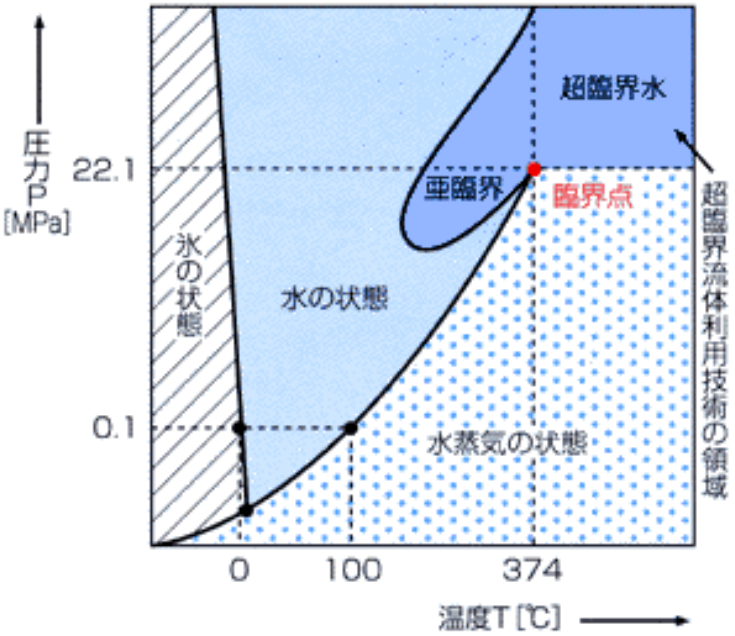
- ✓ 高いイオン積により水自身が酸触媒として働く
- ✓ 高い拡散性をもつ

高速反応が期待できる

超臨界水

（臨界温度 374.2°C, 臨界圧力 22.1 MPa）

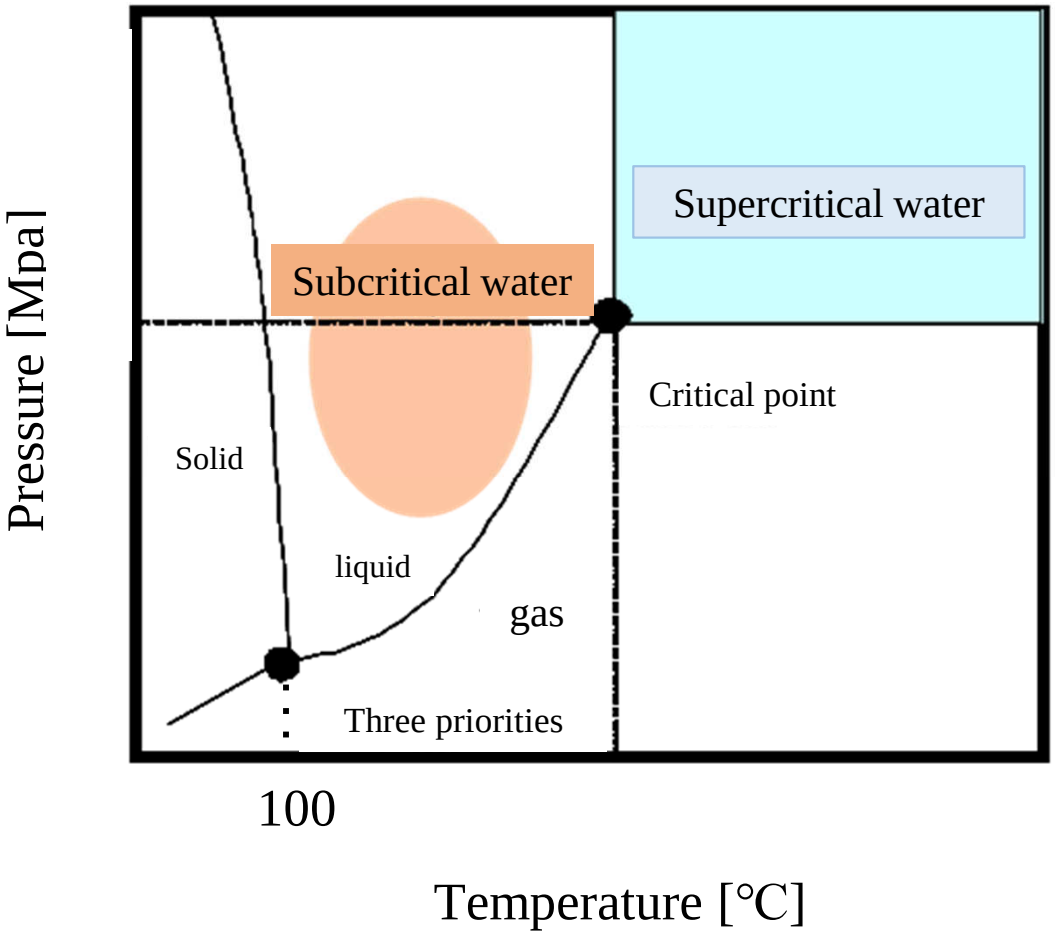


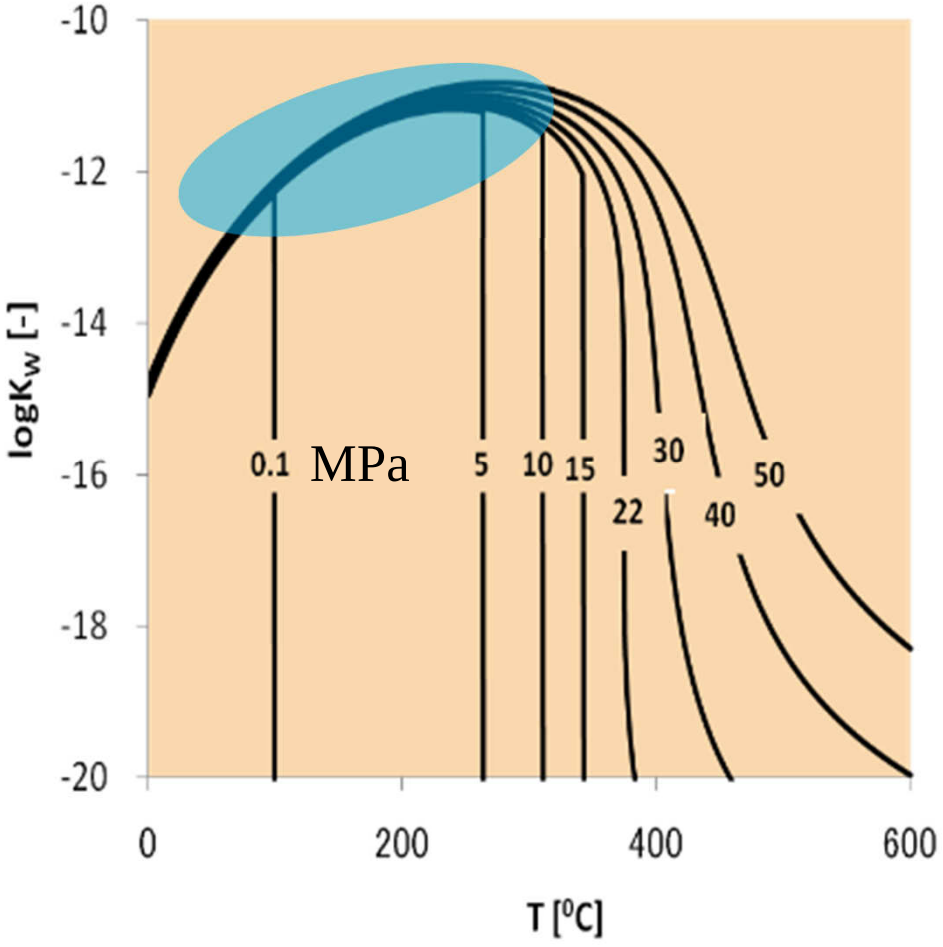


Subcritical water

✓ Water above saturated vapor pressure
✓ Low cost, non-toxic, non-flammable, non-explosive
✓ High ionic product of water, with acid catalytic effect

Protein hydrolysis
Accelerate to degradation





非可食部は高付加価値物質へ変換！

稲ワラ・麦ワラ


作物の果皮類



種子・葉・根茎




油カス

超臨界CO_2抽出，　亜臨界H_2O加水分解など

高付加価値素材

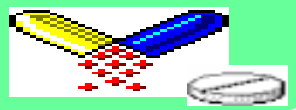
健康食品

カロテノイド，　ビタミン，　植物ステロール



香料・医薬品

フラボノイド，油脂，薬用成分

化学原料 燃料など

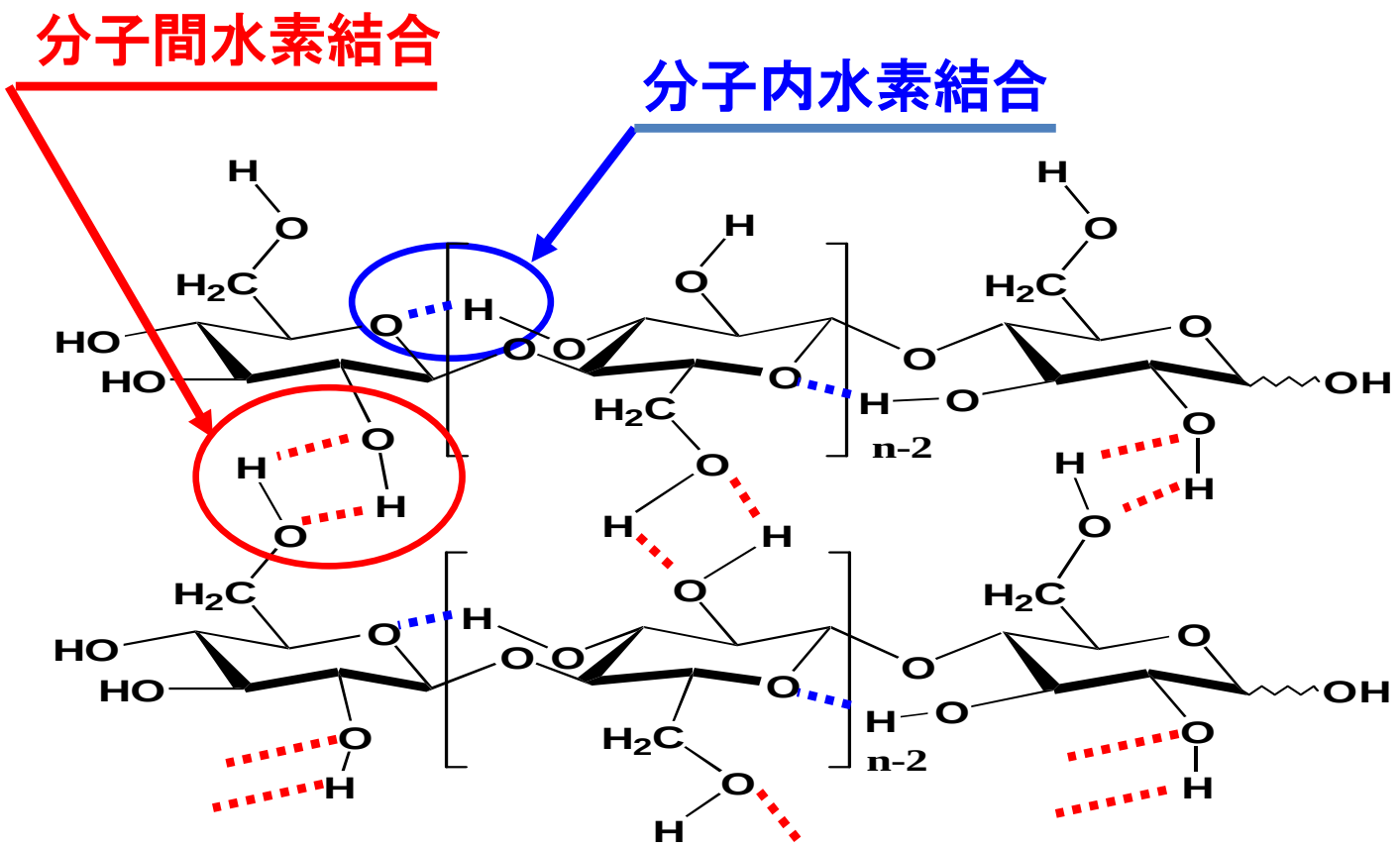
化粧品

テルペノイド/テルペン
芳香族エステル

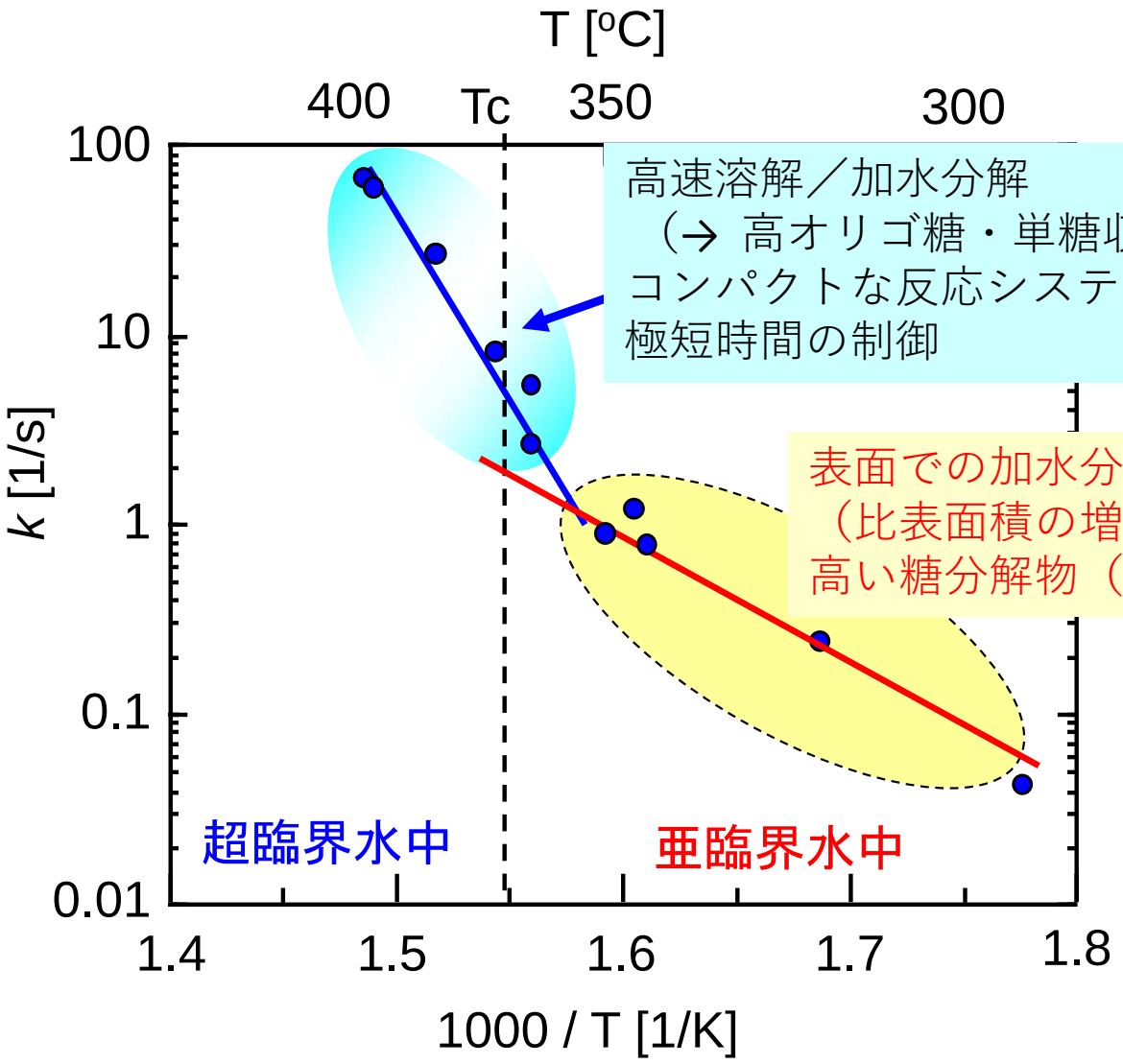
亜臨界水：結晶性ポリマーの溶解（分散）は困難

例. セルロース

高極性のグルコース残基のホモポリマーにもかかわらず，
特殊な溶媒でなければ溶解させることができない
（分子内・間水素結合の発達）



結晶性セルロース分解速度の温度依存性と利用可能な分野について



高速溶解／加水分解
（→ 高オリゴ糖・単糖収率）
コンパクトな反応システム
極短時間の制御

表面での加水分解＋熱分解
（比表面積の増大、表面疎水化？）
高い糖分解物（→炭化物, フラン誘導体）

利用可能な分野

- ✓ 廃棄物処理（無機化）
  （形態：回分式）
- ✓ 液体肥料（低分子量化）
  （形態：回分式、
  流通式マイクロ反応器）

- ✓ 食品分野（抽出前処理）
  （形態：回分式）
- ✓ エネルギー分野（燃料化）
  （形態：回分式）

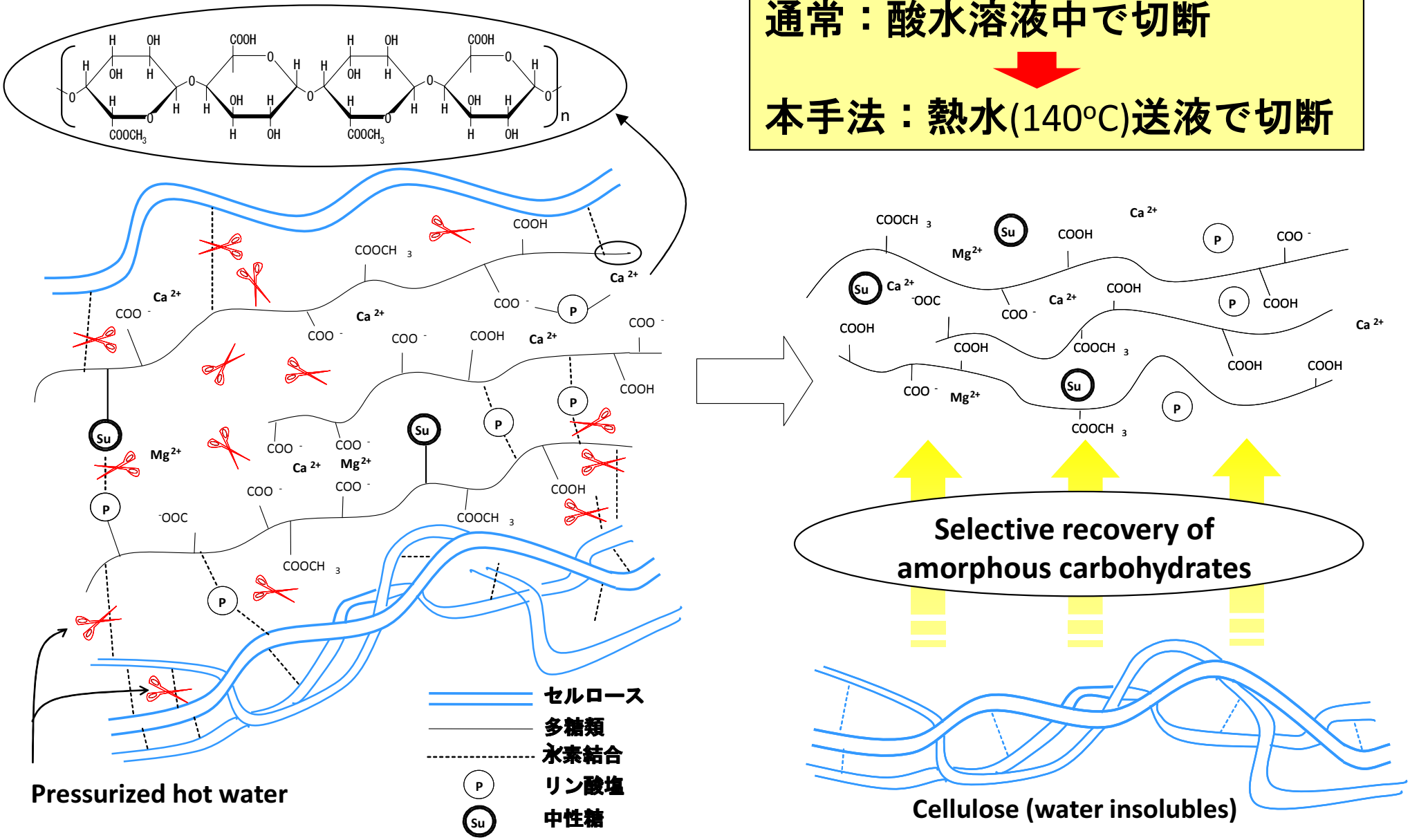
セルロースを固体として回収し、他の成分を溶解・分解等で分離回収するプロセスが現実的

J. Supercrit. Fluids, 1998
Fluid Phase Equilibria, 1999

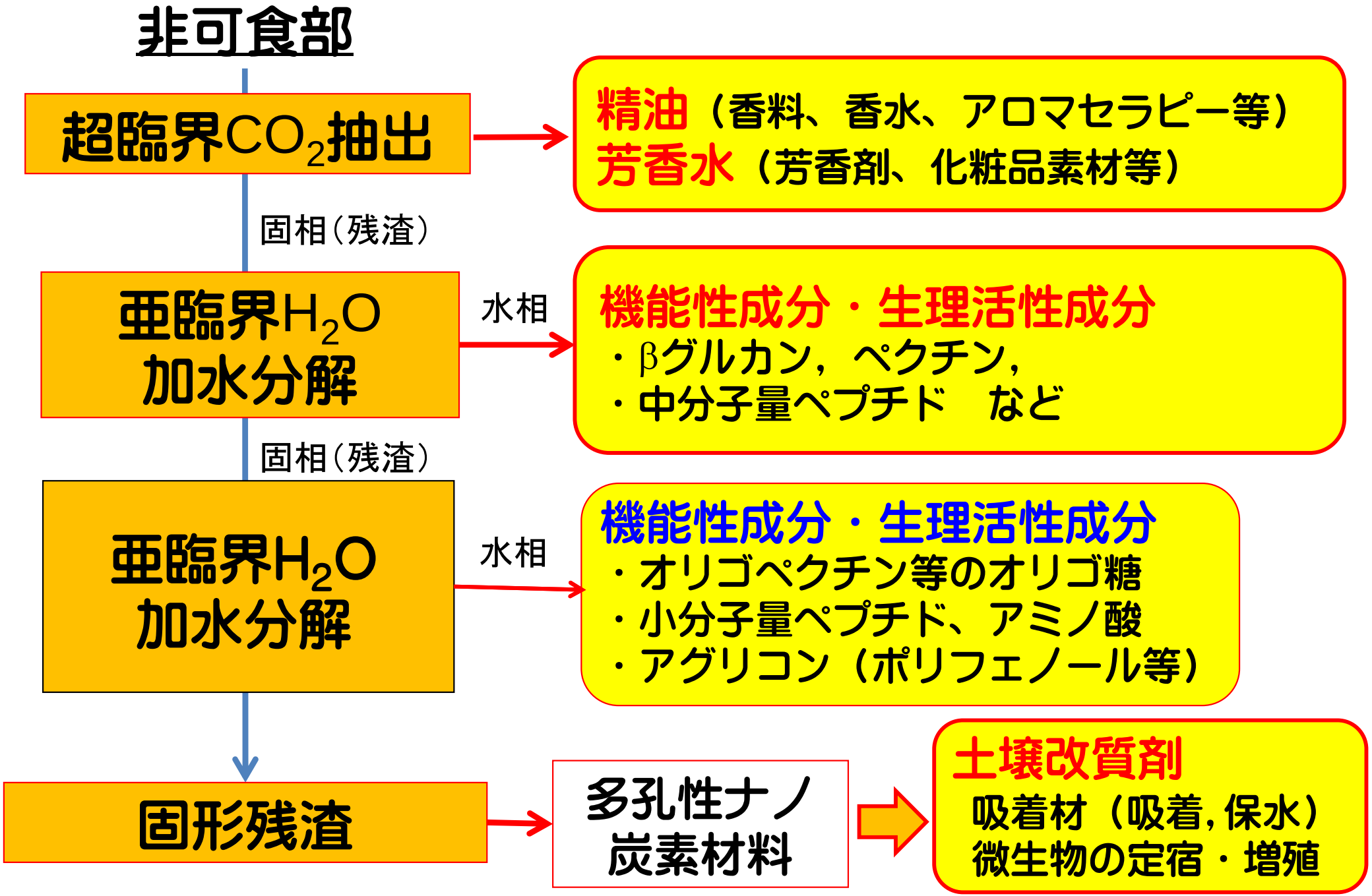
亜臨界水：セルロースとペクチンの相互作用を切断できる
ペクチンの低分子化も可能である

通常：酸水溶液中で切断

本手法：熱水(140°C)送液で切断



亜臨界水でできること


非可食部
超臨界CO_2抽出
精油（香料、香水、アロマセラピー等）
芳香水（芳香剤、化粧品素材等）
固相（残渣）
亜臨界H_2O
加水分解
水相
機能性成分・生理活性成分
・βグルカン，ペクチン，
・中分子量ペプチド　など
固相（残渣）
亜臨界H_2O
加水分解
水相
機能性成分・生理活性成分
・オリゴペクチン等のオリゴ糖
・小分子量ペプチド、アミノ酸
・アグリコン（ポリフェノール等）
固形残渣
多孔性ナノ
炭素材料
土壌改質剤
吸着材（吸着，保水）
微生物の定宿・増殖

村上ら, 化学工学会第53回秋季大会 (2022年9月).

Subcritical water liquefaction of vinegar production residues and their acetic acid fermentation for the development of new vinegar

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Munehiro Hoshino[2, 3] Mitsuru Sasaki[4, 5]

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[3]M&A Food Technology and Biology of Technical Center (M.A.F.T), Japan. [4]Faculty of Advanced Science and Technology, Kumamoto University Japan. [5]Institute of Industrial Nanomaterials, Kumamoto University Japan.

Background

Rice bran and sake lees, which are disposed of in the vinegar production process

Rice-plant

Rice polishing

White and brown rice

Sacchari fication

Sweet sake

Alcohol fermentation

Unrefined sake

Abandonment

3t / year

High protein
High Mineral

Rice bran

Subcritical water treatment

Additives for Vinegar

High amino acid
High Mineral

Abandonment

Sake lees

15t / year

High protein
High Mineral

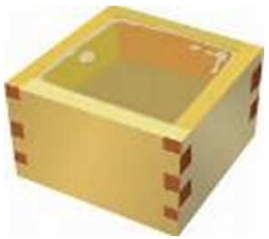
Squeezing

Grain vinegar

Acidification

Acetic acid bacteria feed

Alcohol



Background

Sake lees

Rice bran

Sake lees	Component [g]	Rice bran	Component [g]
Moisture	51.1	Moisture	10.3
Protein	14.9	Protein	13.4
Lipid	1.5	Lipid	19.6
Carbohydrates	29	Carbohydrates	48.8
Mineral content	3.5	Mineral content	7.9

Previous Research [3)]

~Sake lees~

Processing temperature : 120~180℃
Processing time : 30~360min
Liquefaction rate : 41~60%

- The temperature range around 120°C was a good condition.
- Liquefaction rate is low.

~Rice bran~

Processing temperature : 120~180℃
Processing time : 30~360min
Liquefaction rate : 67%

- Cannot decompose at low temperatures.
- Requires processing at high temperatures.

[3)] SCEJ 52rd Autumn Meeting

~Subcritical water treatment for Sake lees [3] ~

Liquefaction rate : 44% (120S240)

Liquefied sake lees [ppm]

Temperature [℃]	Reaction time [min]	Amino acid conc. [ppm]	P [ppm]	K [ppm]	Ca [ppm]	Mg [ppm]
120	240	8125	113	127	21	26

Optimal conditions for sake lees are 120°C for 240 minutes, whereas optimal conditions for rice bran have not been developed.

Need to find optimal conditions for rice bran at high temperatures

[3] SCEJ 52rd Autumn Meeting

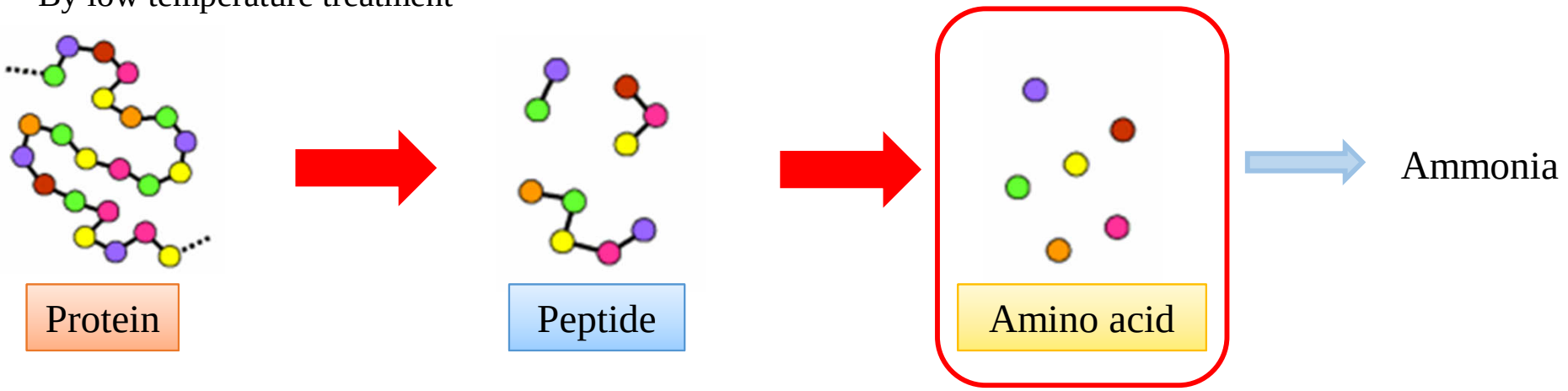
Objectives

- Formulation of subcritical water treatment conditions for rice bran

  → High concentration elution of phosphorus, minerals, and amino acid components

- Acetic acid fermentation test of mixed samples of rice bran and sake lees

By low temperature treatment



Experimental Methods

Experimental Operation

Raw materials+ distilled water 0.3 L

mixing

hydrolysis

Subcritical water treatment

cooling

suction filtration

solid

liquid

desiccation

24h,50℃

pH measurement

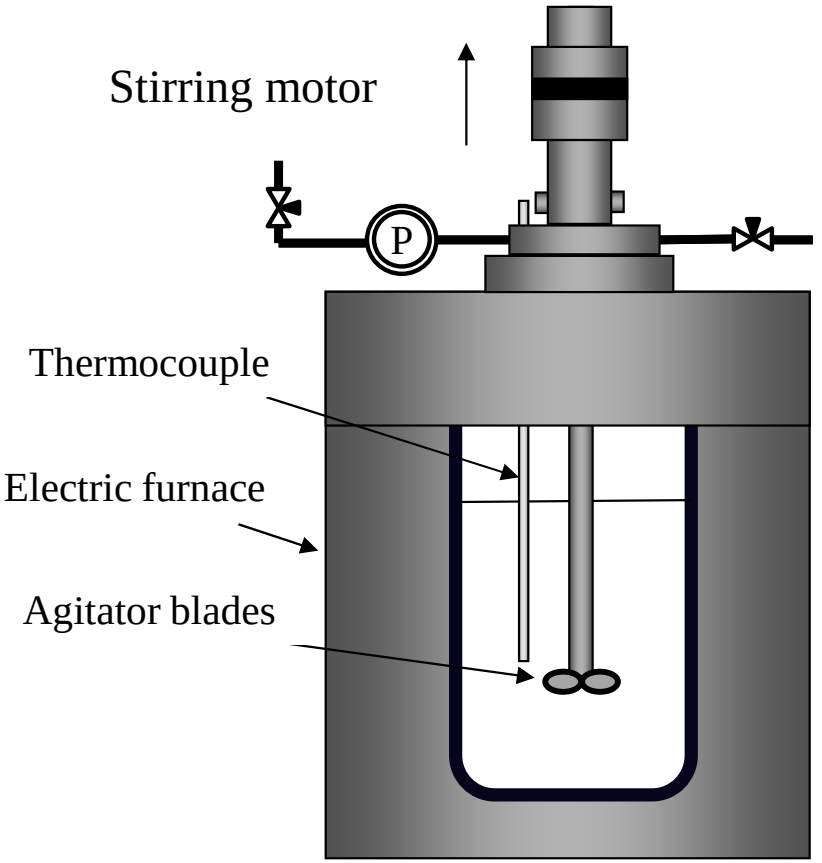
weighing

analysis

Total Nitrogen
Total Amino acids
Ammonia
Phosphorus
Mineral(K, Ca, Mg)

Equipment

Autoclave [SUS-316]



Objectives

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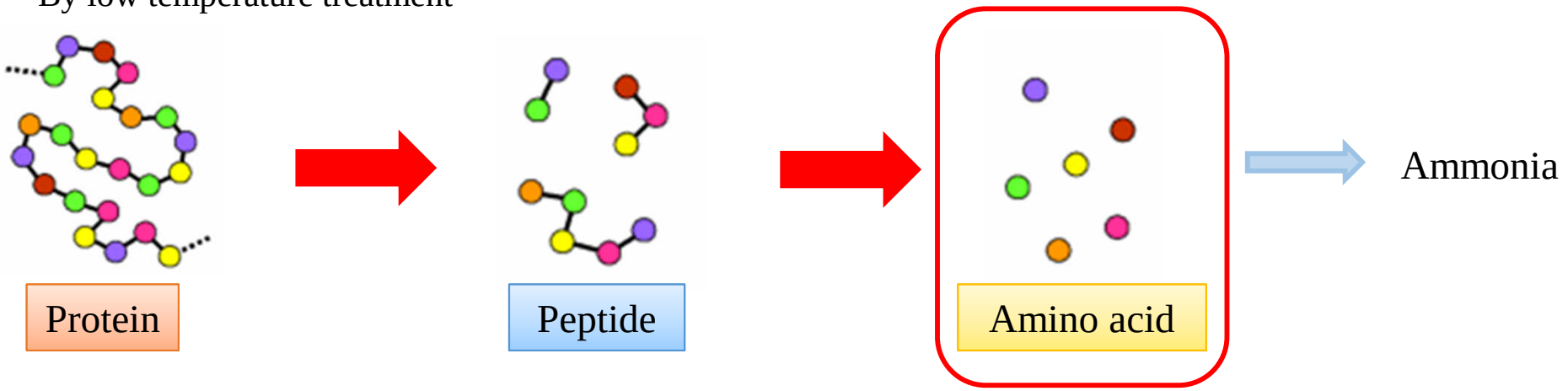

Experimental conditions

Volume of water [mL]	300
Temprature [℃]	200, 220
Time [min]	30
Raw materials [g]	30, 45, 60

180R30 [3] ← Treated at 180°C for 30 minutes

Raw materials [g]	Liquefaction rate [%]	pH
30g	**68.20**	4.78
45g	**69.44**	4.62
60g	**67.17**	4.34

200R30

Raw materials [g]	Liquefaction rate [%]	pH
30g	**66.74**	3.57
45g	**64.19**	3.41
60g	**56.80**	3.26

220R30

Raw materials [g]	Liquefaction rate [%]	pH
30g	**55.74**	3.53
45g	**54.67**	3.63
60g	**48.58**	3.74

Liquefaction rate decreased with temperature

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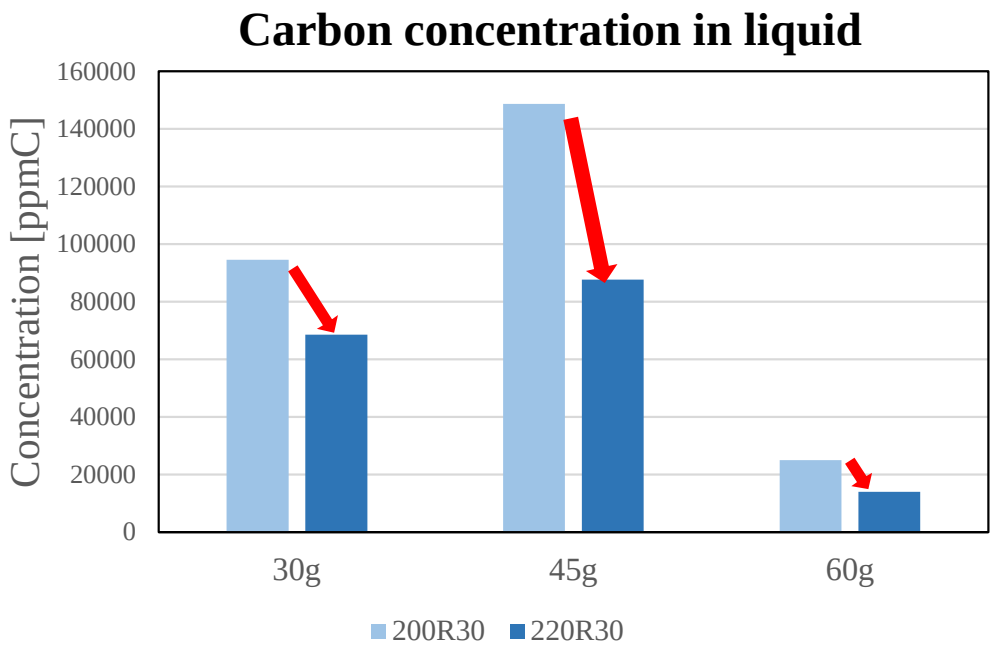
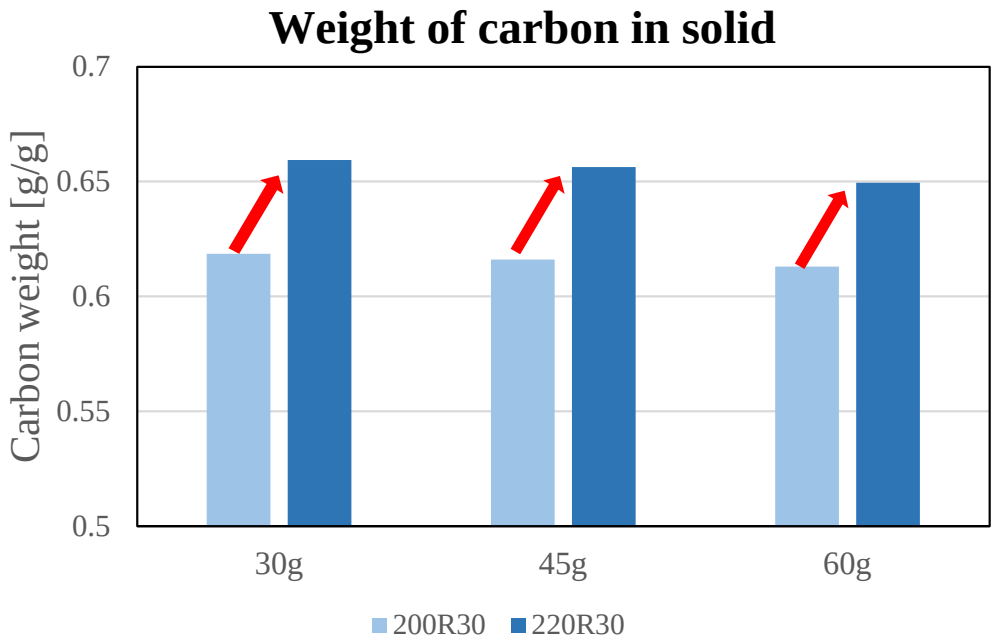
Results & Discussions





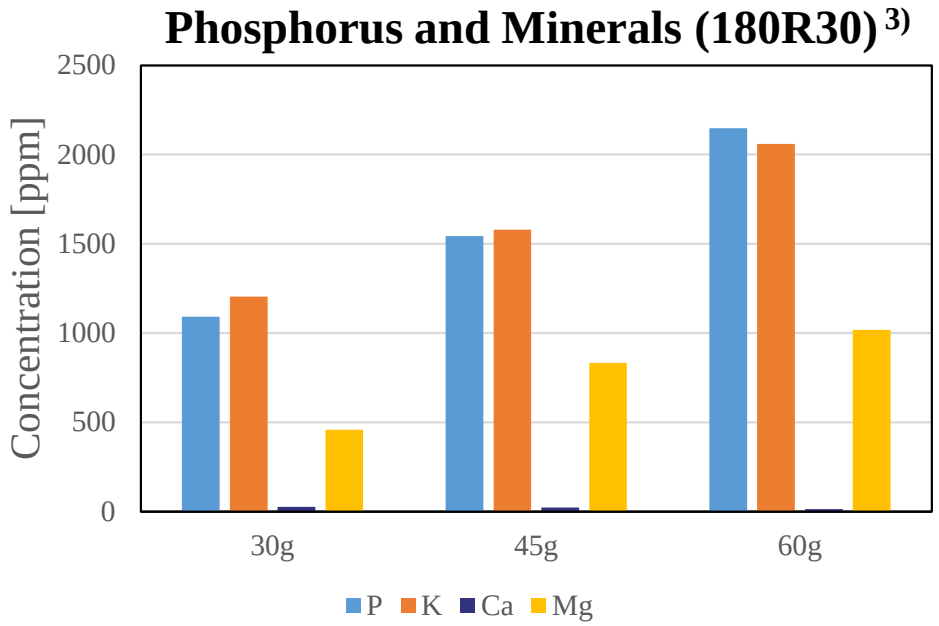
The carbon concentration in the liquid decreased as the treatment temperature increased.

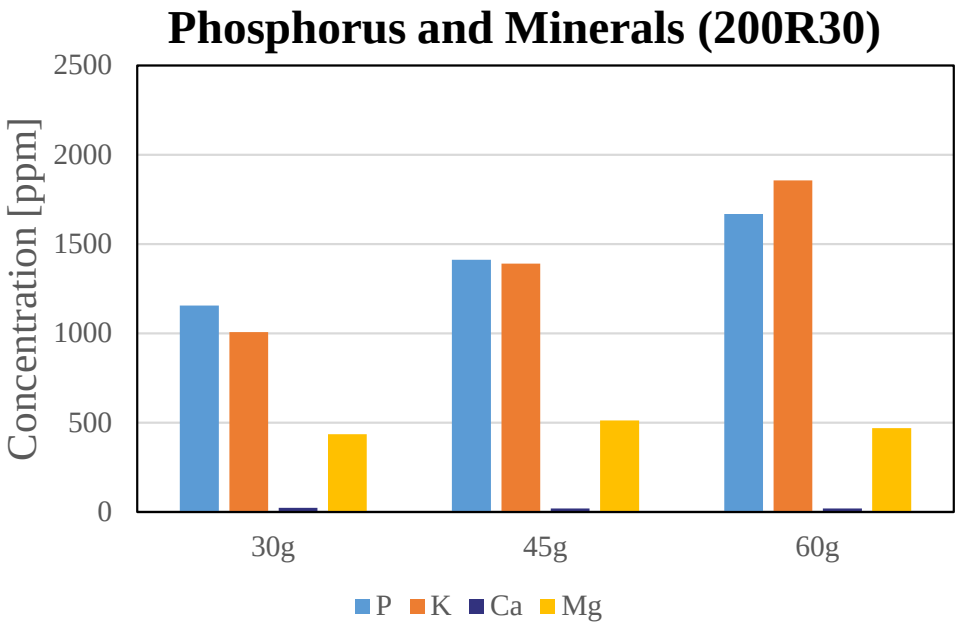
⇩

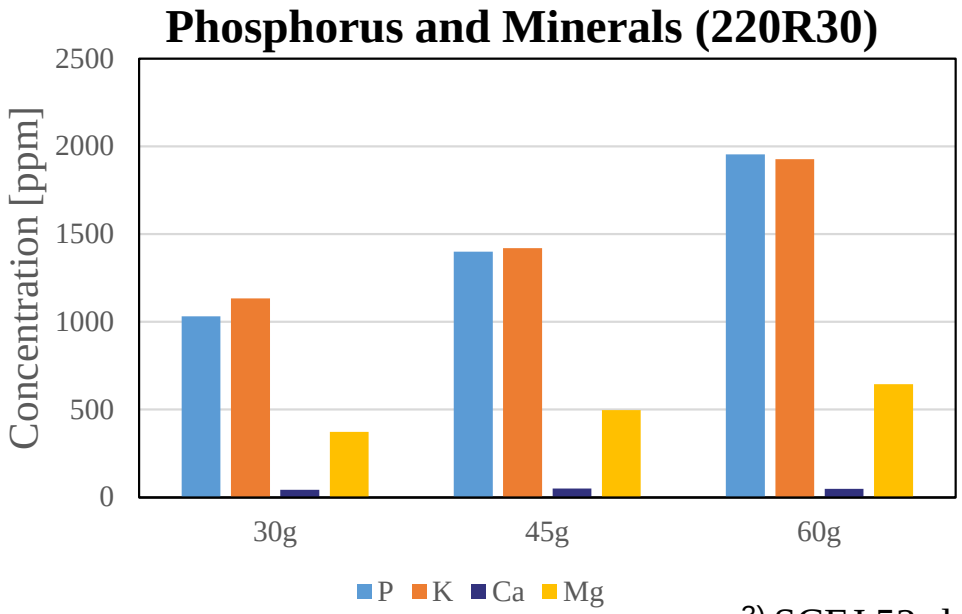
Possible Cellulose carbonization.

⇧

The carbon weight in the solid residue increased as the treatment temperature increased.







Comparing the mineral composition, the treatment at 180°C is the highest. Considering liquefaction efficiency, 180°C is the best condition.

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Experimental condition for high liquefaction rate from rice bran

- Treatment at 180°C has the highest liquefaction rate.

180R30

Raw materials [g]	Liquefaction rate [%]	pH
30g	**68.20**	4.78
45g	**69.44**	4.62
60g	**67.17**	4.34

Temperature [°C]	Reaction time [min]	Amino acid [ppm]	P [ppm]	K [ppm]	Ca [ppm]	Mg [ppm]
180	30	308	1544	1580	22	834

- Suitable operating conditions for high liquefaction rate:

180°C, 30 min, 45 g-material/ 300 mL-H_2O

Objectives

- Formulation of subcritical water treatment conditions for rice bran

  → High concentration elution of phosphorus, minerals, and amino acid components

- Acetic acid fermentation test of mixed samples of rice bran and sake lees

By low temperature treatment

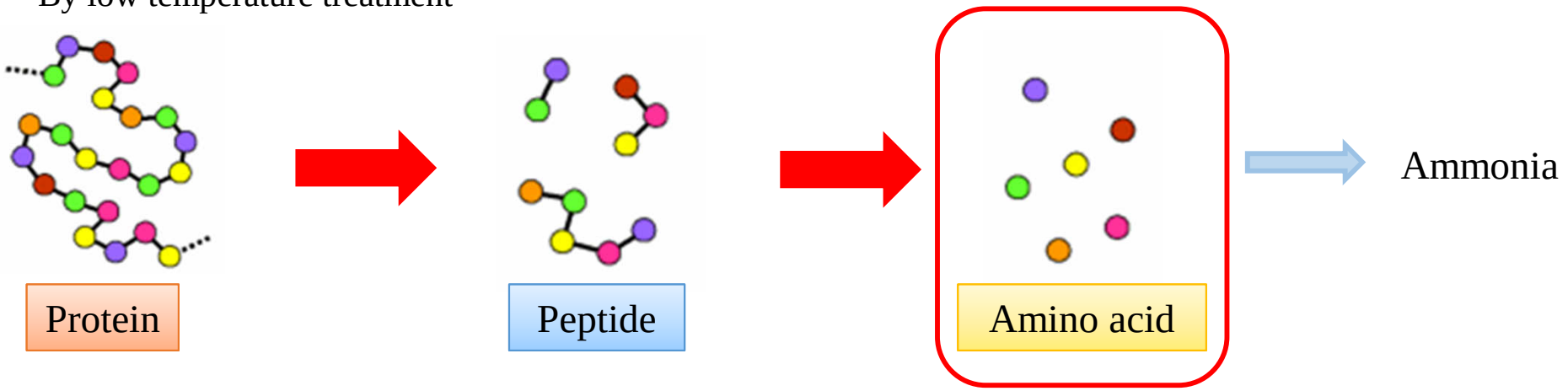

Table. Comparison with commercial products [ppm] [3)]

	Amino acid conc.	P	K	Ca	Mg
Sake lees vinegar (120S240)	5753	289	118	19	38
Black vinegar (Company B)	3684	1021	1166	93	282

✓ The amino acid component is higher than that of black vinegar and rice black vinegar, which is a good result.

Liquefied rice bran [ppm]

Temperature [°C]	Reaction time [min]	Amino acid conc.	P	K	Ca	Mg
180	30	308	1544	1580	22	834

✓ Rice bran is rich in phosphorus and minerals. Aiming to use rice bran as a phosphorus and mineral provider.

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Experimental Methods

Rice bran and sake lees, which are disposed of in the vinegar production process

Rice-plant

Rice polishing

White and brown rice

Saccharification

Sweet sake

Alcohol fermentation

Unrefined sake

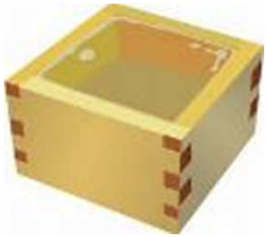
Squeezing

Additives for Vinegar

Trial conditions

120S240＋180R30

Alcohol



Acidification　　Acetic acid bacteria feed

Grain vinegar

Experimental Methods

Acetic acid fermentation process

Rice bran (180℃30min) : Sake lees (120℃240min) ＝ 1 : 1 (Total : 1L)

Liquefied product

180R30＋120S240

Add alcohol and acetic acid bacteria

Acetic acid fermentation

3 days

Static fermentation

Vinegar

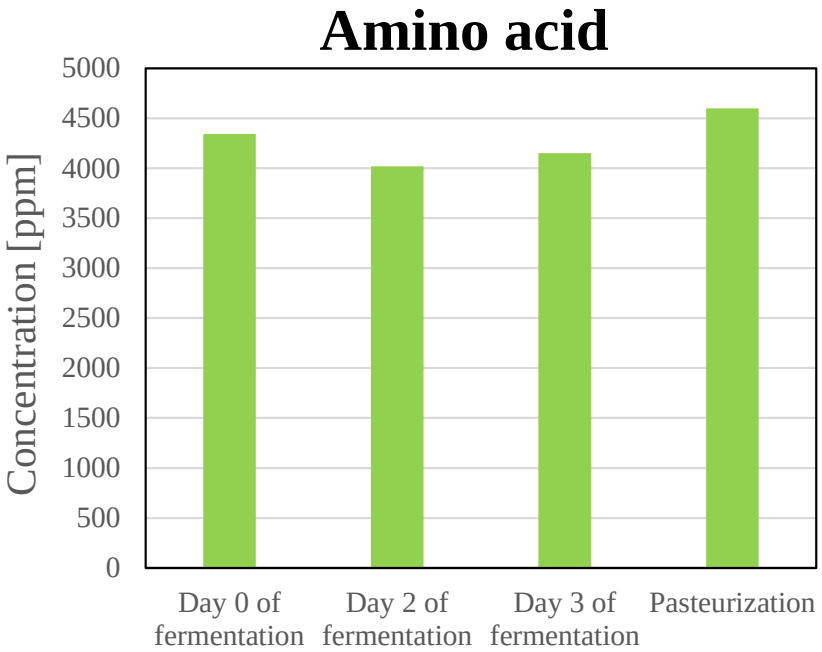
Analysis Item

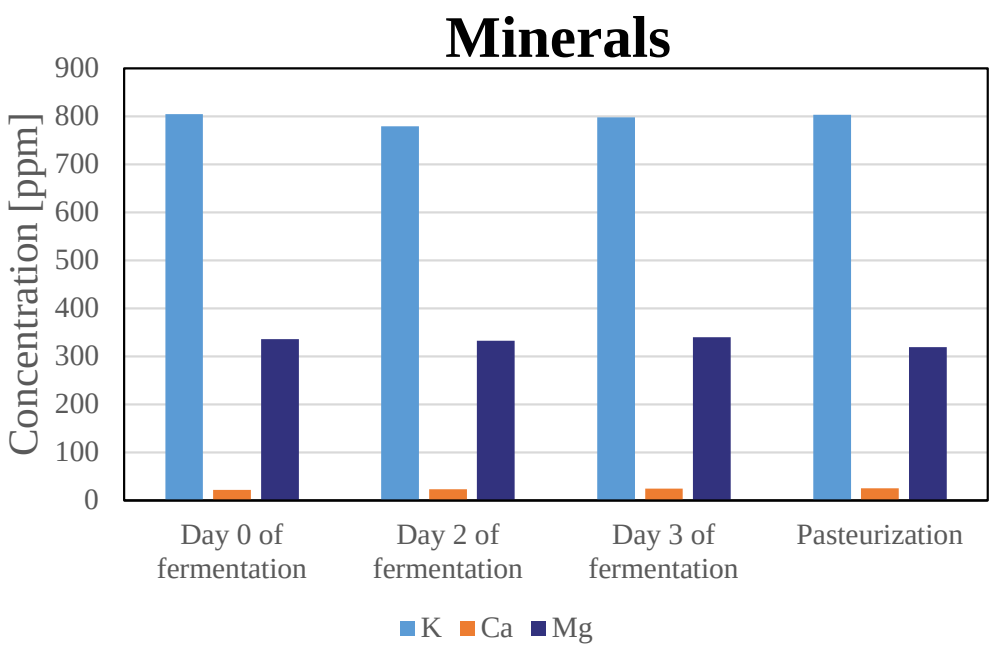
Total nitrogen : TN
Total amino acids
Ammonia : NH_4-N
Phosphorus : P
Minerals(K, Ca, Mg)

Table. Test results for blended and sake lees vinegars

	Energy [kcal]	Protein [g]	Lipids [g]	Carbohydrate [g]	Mineral content [g]	Acidity [%]
Blended vinegar	34	1.4	0.0	8.3	0.4	4.68
Sake lees vinegar (120S240)	25	1.7	0.0	5.7	0.1	4.39
Grain vinegar	25	0.3	0.0	7.0	-	4.20

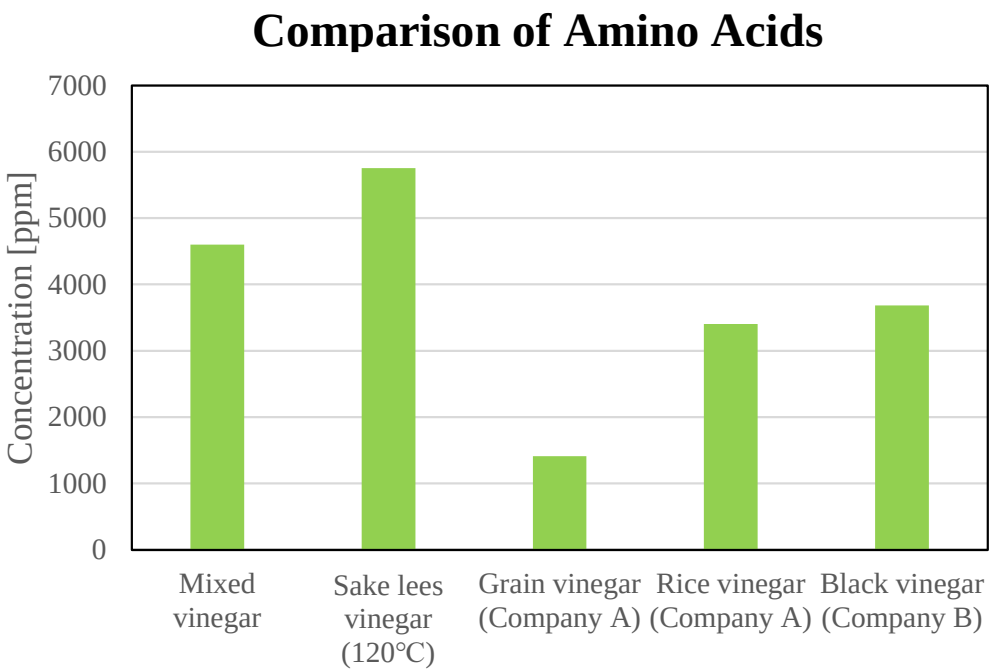
Behavior of each component in the fermentation process

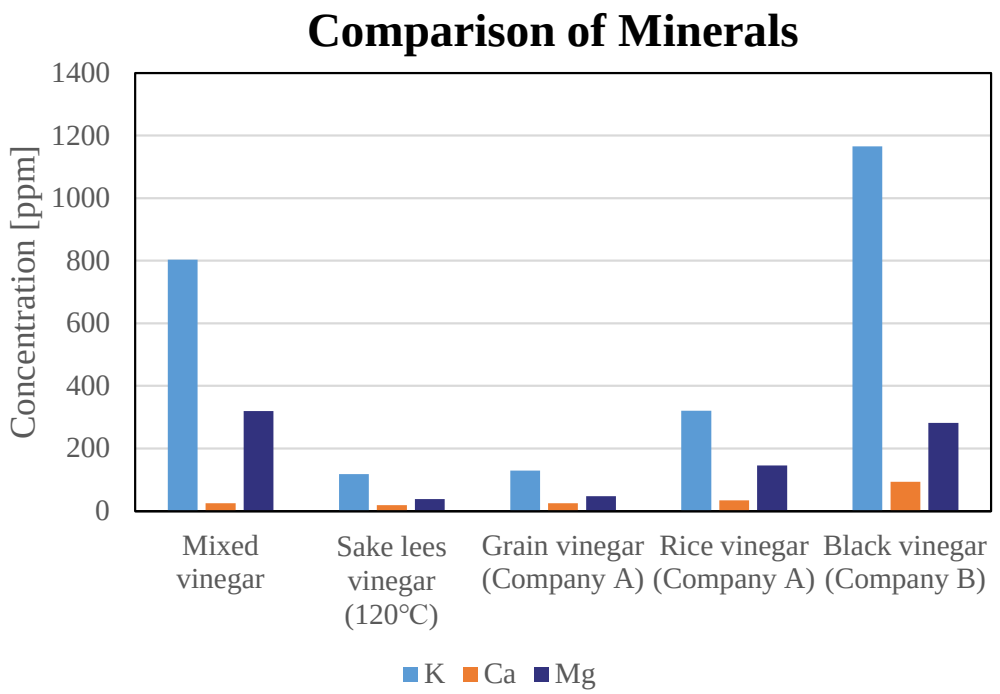




Amino acids were present without loss during the fermentation and fire-working processes.

Mineral content was not lost during the fermentation and pasteurization process.





We have succeeded in producing a vinegar rich in amino acids, with an amino acid composition higher than that of common grain vinegar, rice black vinegar, and black vinegar. In addition, the mineral component was greatly improved compared to black vinegar. Amino acids and minerals in rice bran and sake lees existed without interfering with each other during the fermentation process.

Table. Comparison with commercial products [ppm]

	Amino acid	K	Ca	Mg
Blended vinegar (180R30 + 120S240)	4599	803	26	319
Sake lees vinegar (120S240)	5753	118	19	38
Grain vinegar (Company A)	1412	129	25	47
Rice vinegar (Company A)	3405	320	34	146
Black vinegar (Company B)	3684	1166	93	282

- The amino acid content was also higher than that of the commercial product, and the mineral content was also improved.
- Ingredients can be manipulated by changing the mixing ratio of sakekasu and rice bran.

Conclusions

~Subcritical water treatment~

180R30

Raw materials [g]	Liquefaction rate [%]	pH
30g	**68.20**	4.78
45g	**69.44**	4.62
60g	**67.17**	4.34

Temperature [°C]	Time [min]	Amino acid	P	K	Ca	Mg
180	30	308	1544	1580	22	834

~Vinegar production~

Acidity :
4.68%

	Amino acid	**K**	**Ca**	**Mg**
Mixed vinegar	**4599**	**803**	**26**	**319**

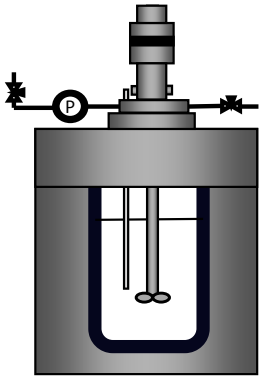
Rice bran was found to be best under the condition of 180°C for 30 minutes. In addition, mixed vinegar of rice bran and sake lees yielded high concentrations of both amino acids and mineral components.

これまでの実施例

農林水産資材



超臨界・亜臨界
H_2O / CO_2
抽出／反応／分離




有価物
機能性成分

香酸柑橘果皮 （例. カボス, 橙）	140°C, 流量1～3 mL/min 半回分式（通水 10min）	（液）ポリフェノール類、ペクチン （固）セルロース（綿状）
大型藻類 （例. ノリ・ワカメ）	120-180°C 回分式（10-30 min）	（液）ポルフィラン（硫酸多糖） （固）固体酸触媒, 吸着剤 etc.
フラボノイド配糖体 （例. ルチン）	160-200°C (w/ GO, マイクロ波) 回分式（15-60 min）	（液）ケルセチン（抗酸化剤） グルコース + ラムノース（糖）
酢製造残渣 （酒粕、米ヌカ）	①140°C, 2-4h (酒粕)　②酢酸発酵 180°C, 2h（米ヌカ） 回分式　40°C, 3d	（液）水溶性ペプチド、アミノ酸、ミネラル （固）残渣（タンパク質含有）

亜臨界水、超臨界二酸化炭素でできること
（ゴミゼロ社会の実現に向けて）

非可食部

超臨界CO_2抽出 → **精油**（香料、香水、アロマセラピー等）
芳香水（芳香剤、化粧品素材等）

亜臨界H_2O 加水分解 → **機能性成分**
・βグルカン，ペクチン，機能性オリゴ糖
・中分子量ペプチド，アミノ酸
・ポリフェノール，配糖体　等

[　　] ⇢ 機能性物質（医薬・化粧品素材），化成品素材，バイオ燃料など

亜臨界水炭化 超臨界CO_2賦活化 → 多孔性ナノ炭素材料 → **土壌改質剤**
吸着材（吸着，保水）
微生物の定着・増殖

ご清聴ありがとうございました

超臨界CO_2、亜臨界・超臨界H_2Oの利用法についてアイディアがあれば是非共同研究しましょう！
さまざまな分野で超臨界流体を用いた基盤研究が展開できればと考えています。

ご質問やご相談があれば、遠慮なくご連絡ください。

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