2015

On-line analysis of catalytic biomass products using a high pressure Tandem mirco-Reactor GC/MS

M. Soll
Frontier Laboratories

R.R. Freeman
Frontier Laboratories

Chu Watanabe
Frontier Laboratories

Ichi Watanabe
Frontier Laboratories

Y.M Kim
Frontier Laboratories

See next page for additional authors

Authors
M. Soll, R.R. Freeman, Chu Watanabe, Ichi Watanabe, Y.M Kim, N. Teramae, and K. Wang

On-line analysis of catalytic biomass products using a high pressure Tandem mirco-Reactor GC/MS

M. Soll[1)], R.R. Freeman[1)], Chu Watanabe[1)], Ichi Watanabe[1)], Y. M. Kim[1)], N. Teramae[2)] and K. Wang[3)]

Frontier Laboratories[(1)], Tohoku University[(2)] and Iowa State University[(3)]

Biorefinery I: Chemicals and Materials From Thermo-Chemical Biomass Conversion and Related Processes

September 27-October 2, 2015
Atlantica Caldera Crete Paradise Hotel
Chania (Crete), Greece

“Almost everything in your daily life depends on catalysts.” – Argonne National Laboratory

- **Continuous search for new catalysts and “good” biomasses** – one that works “better” than those being used for a given process

- **Test parameters**

  Temperature
  Surface area (contact time)
  Atmosphere
  Pressure
  Effective life time
  Activity regeneration

- **Rapid screening of new catalysts (and biomasses) is essential if sustainable “green” products are going to exist in the future.**

FRONTIER LAB

Dimensions for "Rapid screening"

~~Think big !~~

~~Think smal !~~

Think „smart": fast, flexible, µ scale, online GC/MS analysis !

FRONTIER LAB

Fast pyrolysis: Important features for GC/MS

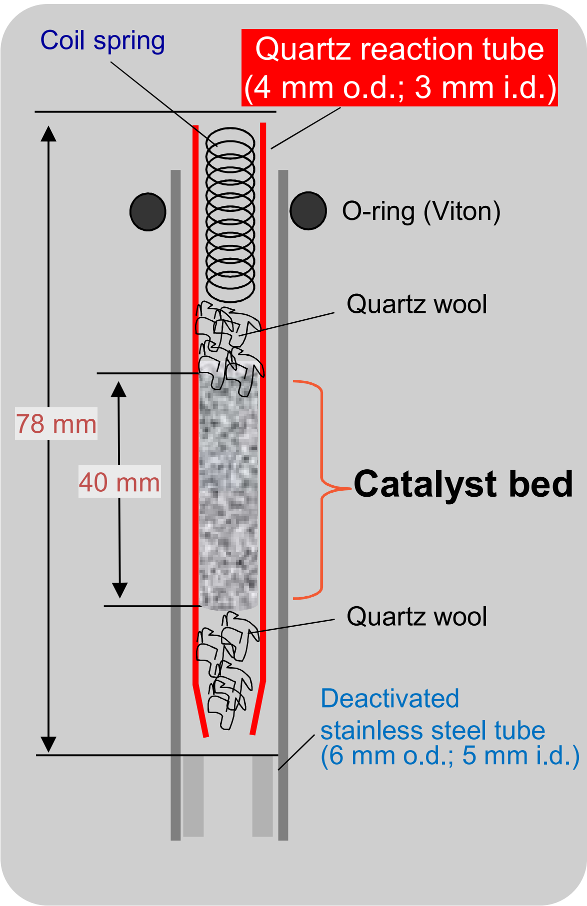
Pyrolyzers and μ-Reactors

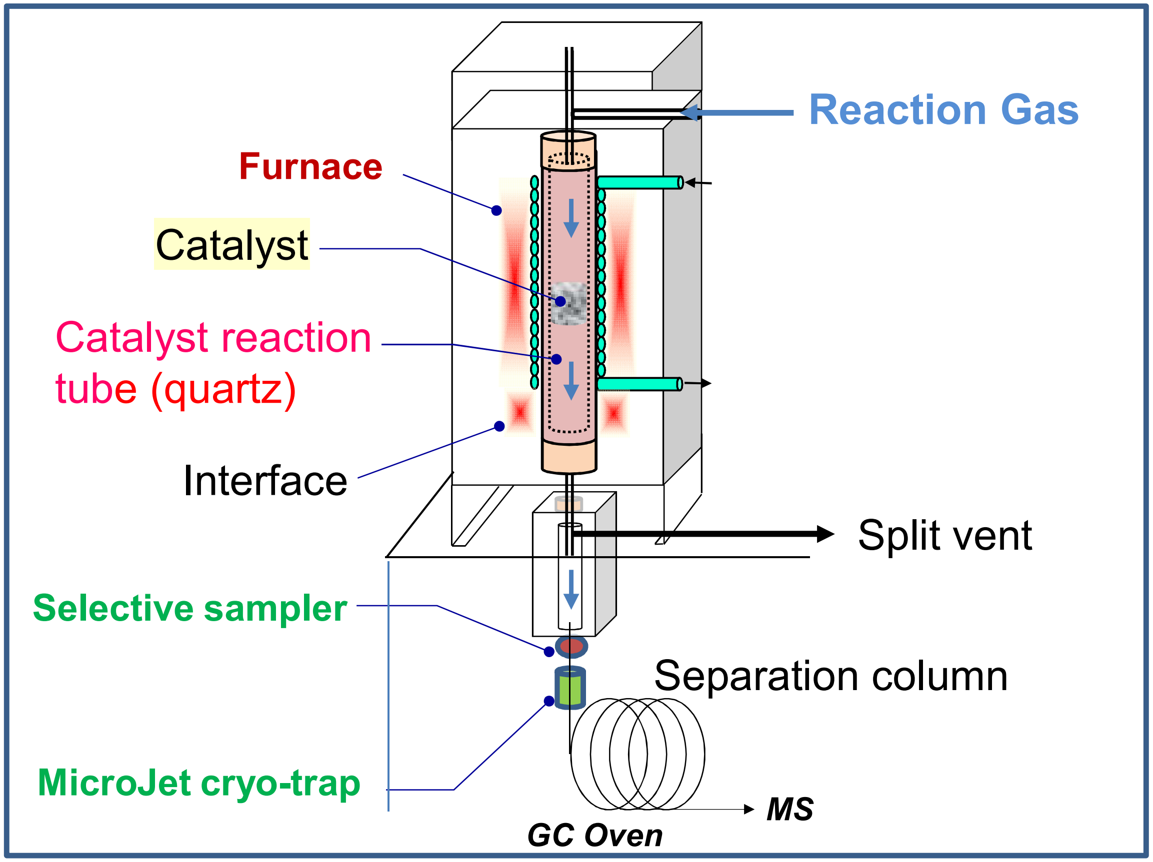
Sample Conditioning

- Gases, liquids and solids → vapors
- Precise Temperature Control
- Low dead volume
- Inert surfaces
- No cold or hot spots

FRONTIER LAB

Design of Single μ-Reactor





FRONTIER LAB

From Single to Tandem μ-Reactor

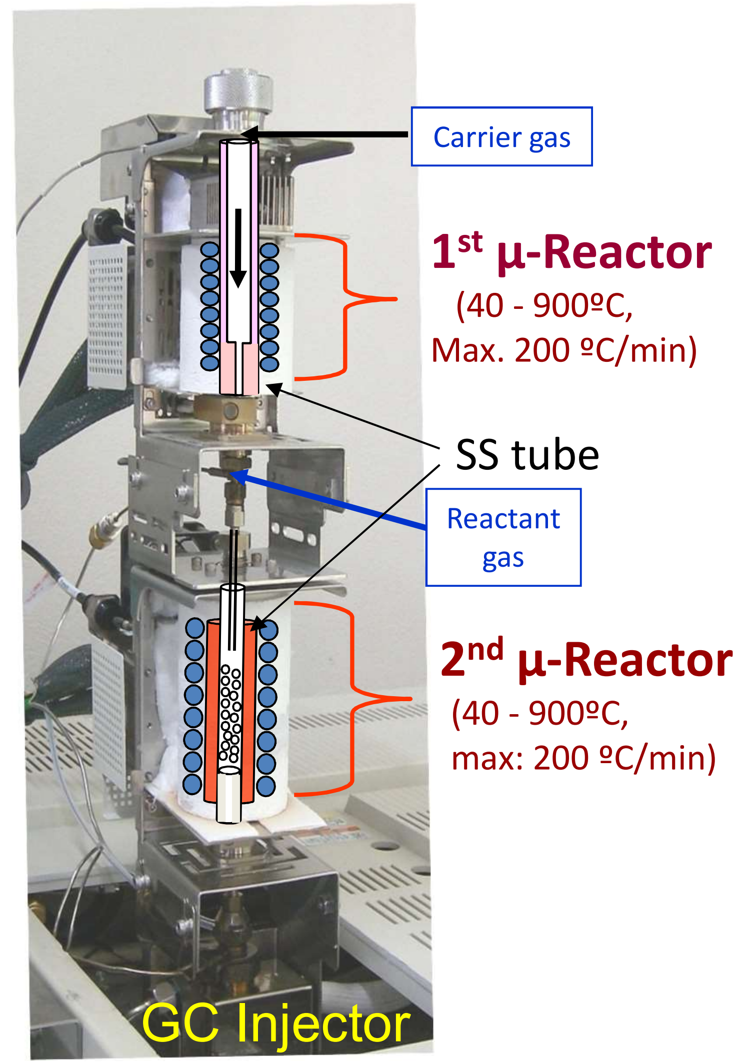
Single μ-Reactor
Rx-3050SR

In-situ only

Tandem μ-Reactor
Rx-3050TR

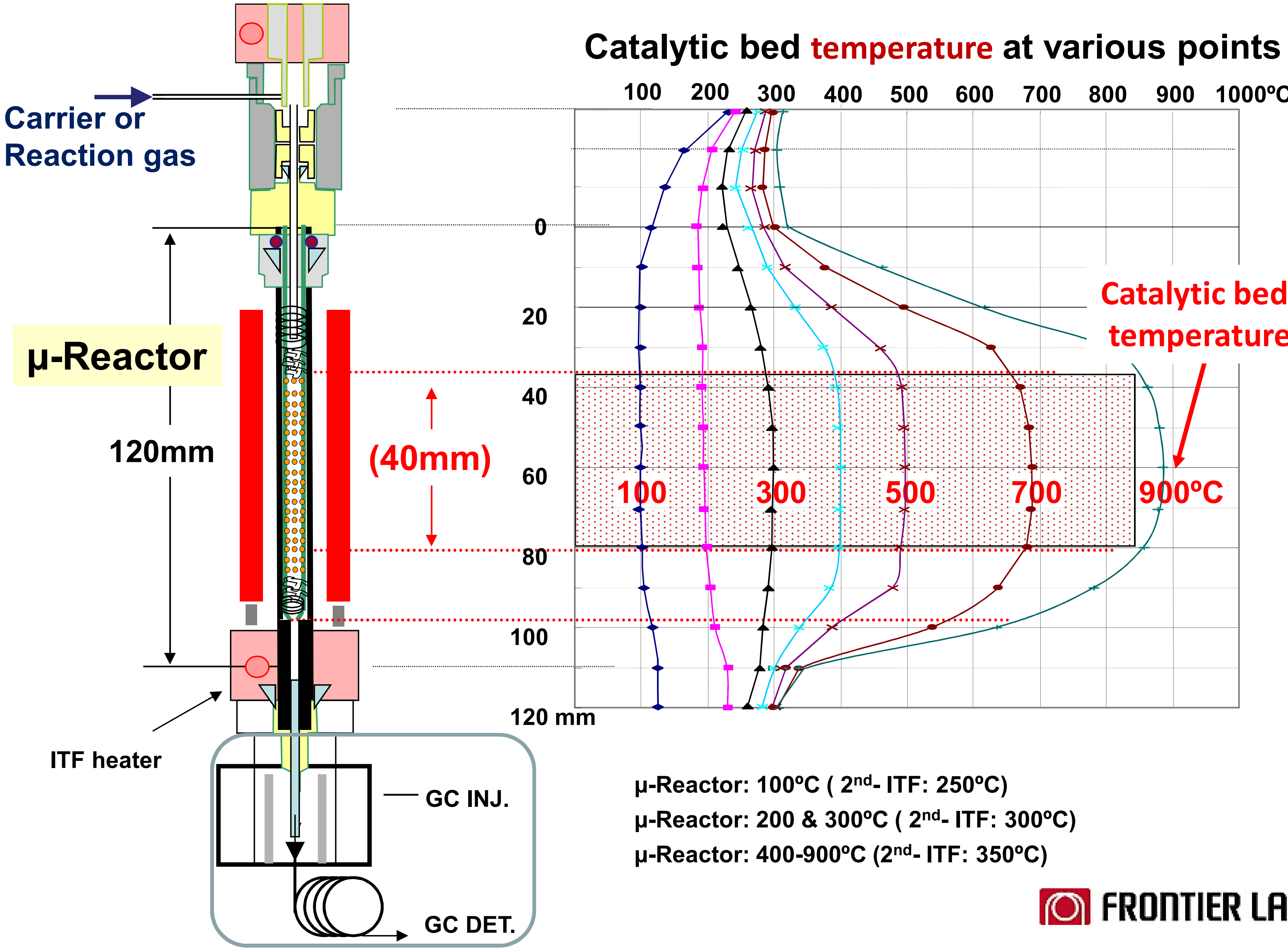
In-situ and ex-situ

- **Catalytic pyrolysis**
- **Catalytic cracking**
- **Hydropyrolysis**
- **High pressure pyrolysis**



FRONTIER LAB

Catalytic bed temperature profiles [100 - 900°C]



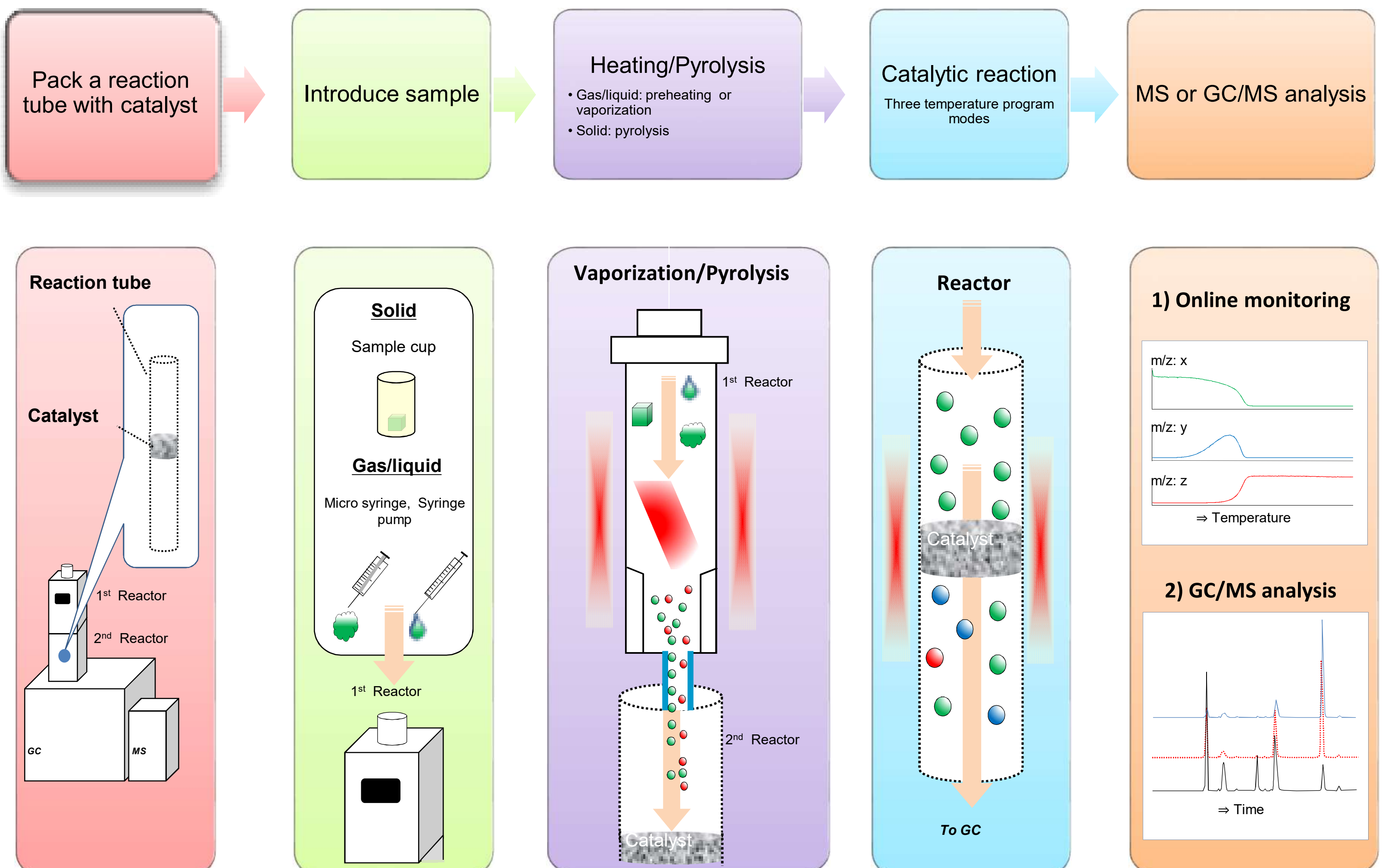
μ-Reactor: 100°C (2nd- ITF: 250°C)

μ-Reactor: 200 & 300°C (2nd- ITF: 300°C)

μ-Reactor: 400-900°C (2nd- ITF: 350°C)

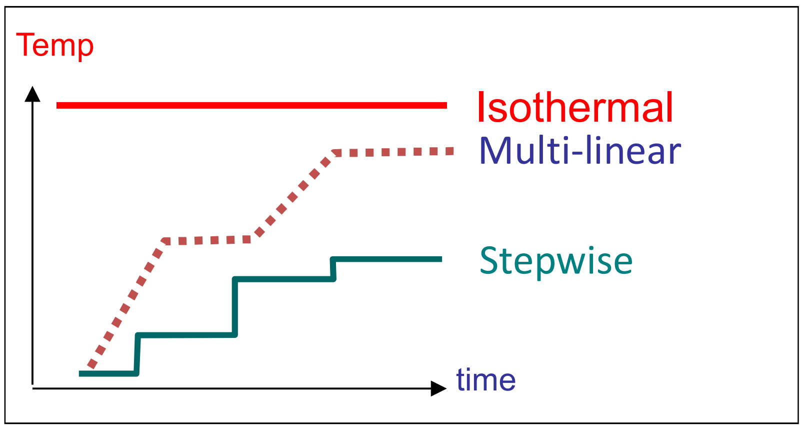
FRONTIER LAB

Handling and workflow

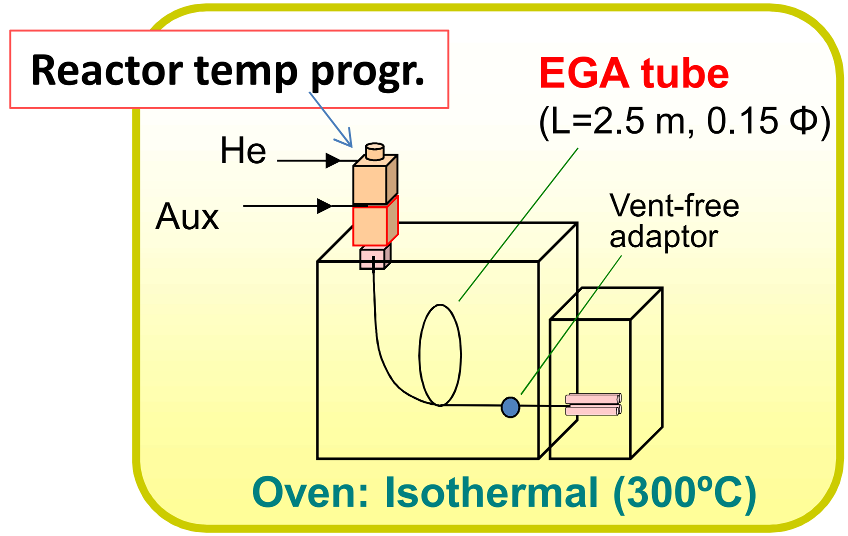


Temperature control and two analytical modes of Tandem μ-Reactor

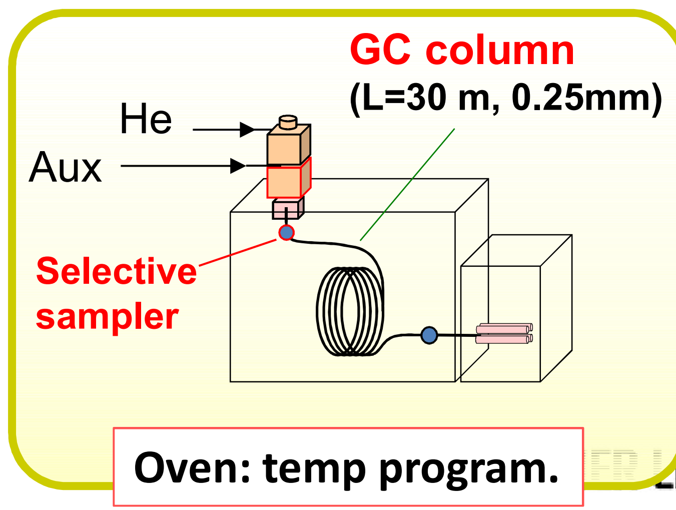
3 Reactor heating profiles



On-line EGA-MS analysis



EGA-Selective zone GC/MS analysis

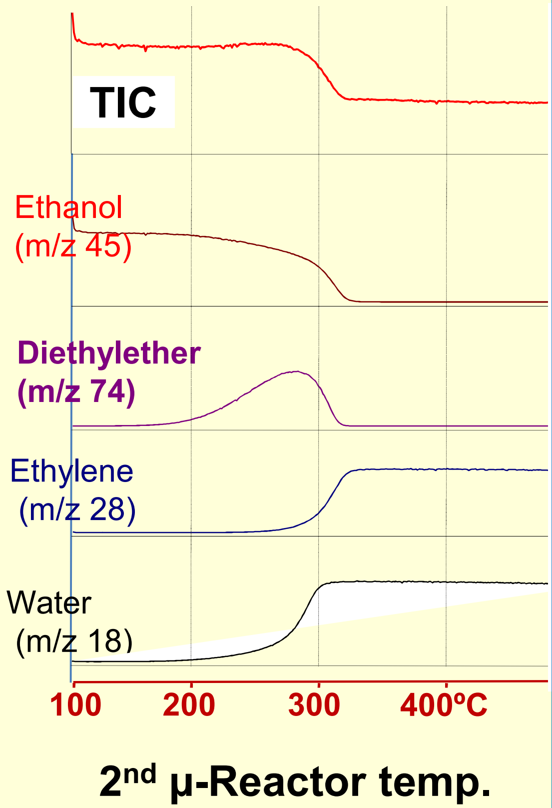


Catalytic conversion of ethanol to ethylene

(Std. config = low pressure)

Online – MS analysis
“ Linear temp. mode ”

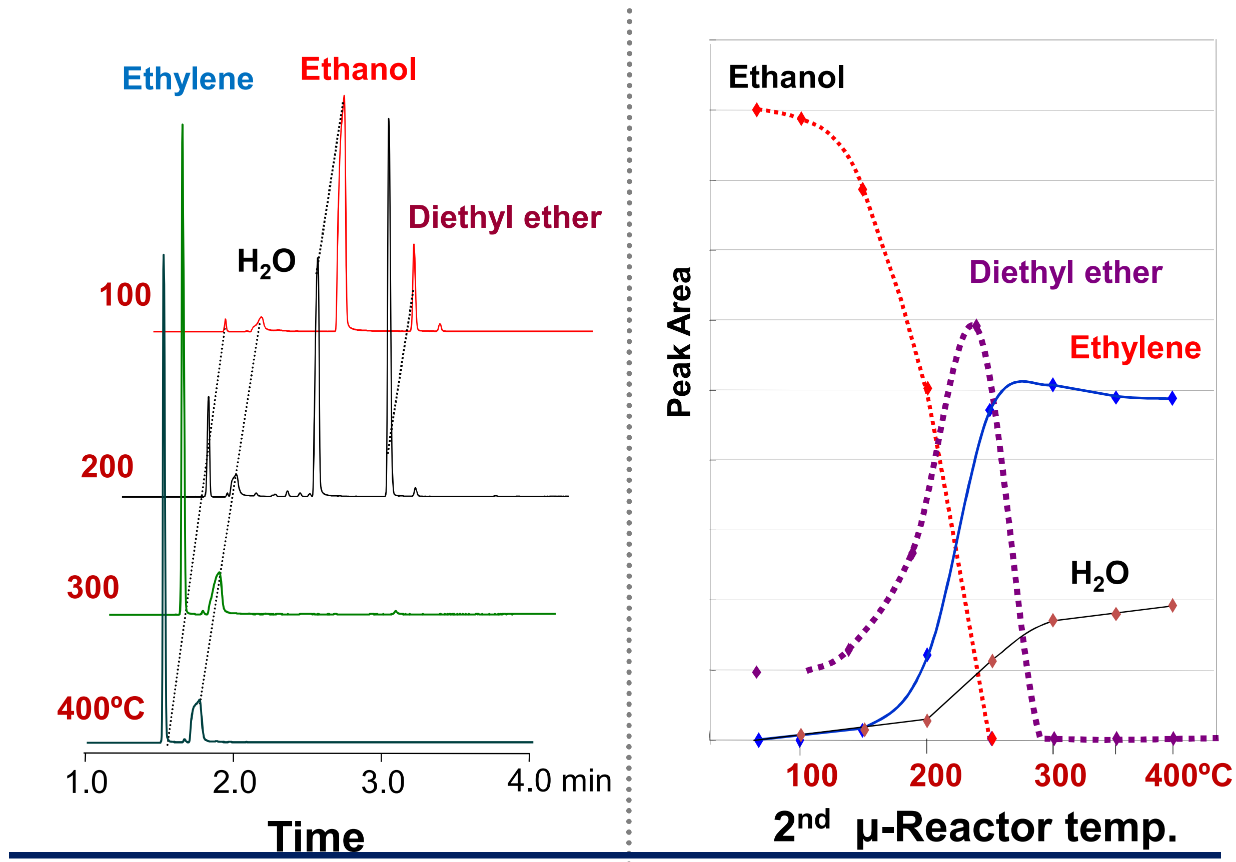
1st μ-Reactor: 100ºC,
2nd μ-Reactor: 100-400ºC (20 ºC/min)
Catalyst: H-ZSM-5



Separation analysis
“ Stepwise temp. mode ”

1st μ-Reactor: 100ºC,
2nd μ-Reactor: 100, 200, 300, 400ºC (1sec)

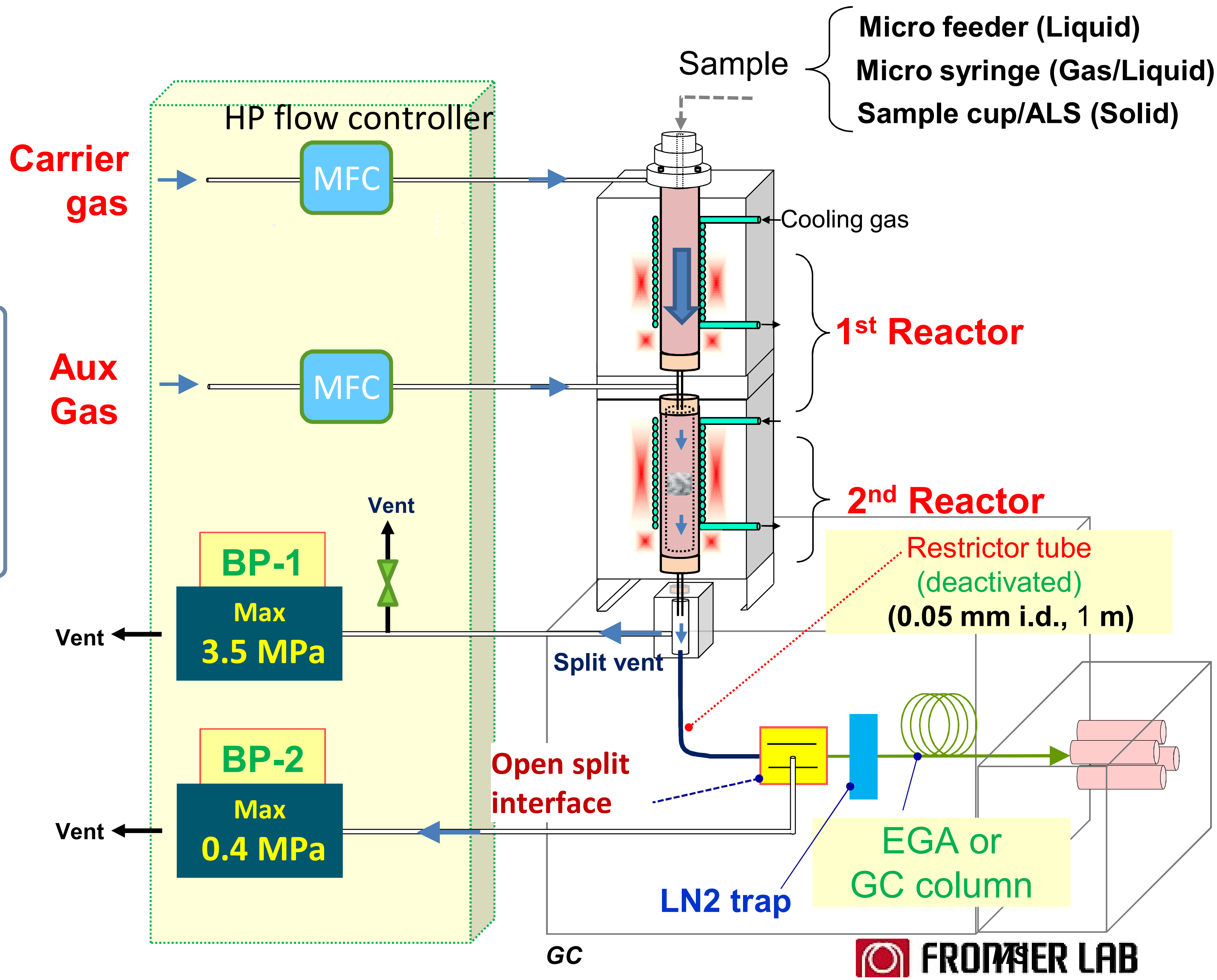
Reaction temp. vs. Peak area



FRONTIER LAB

Innovative pneumatics for HP Tandem μ-Reactor

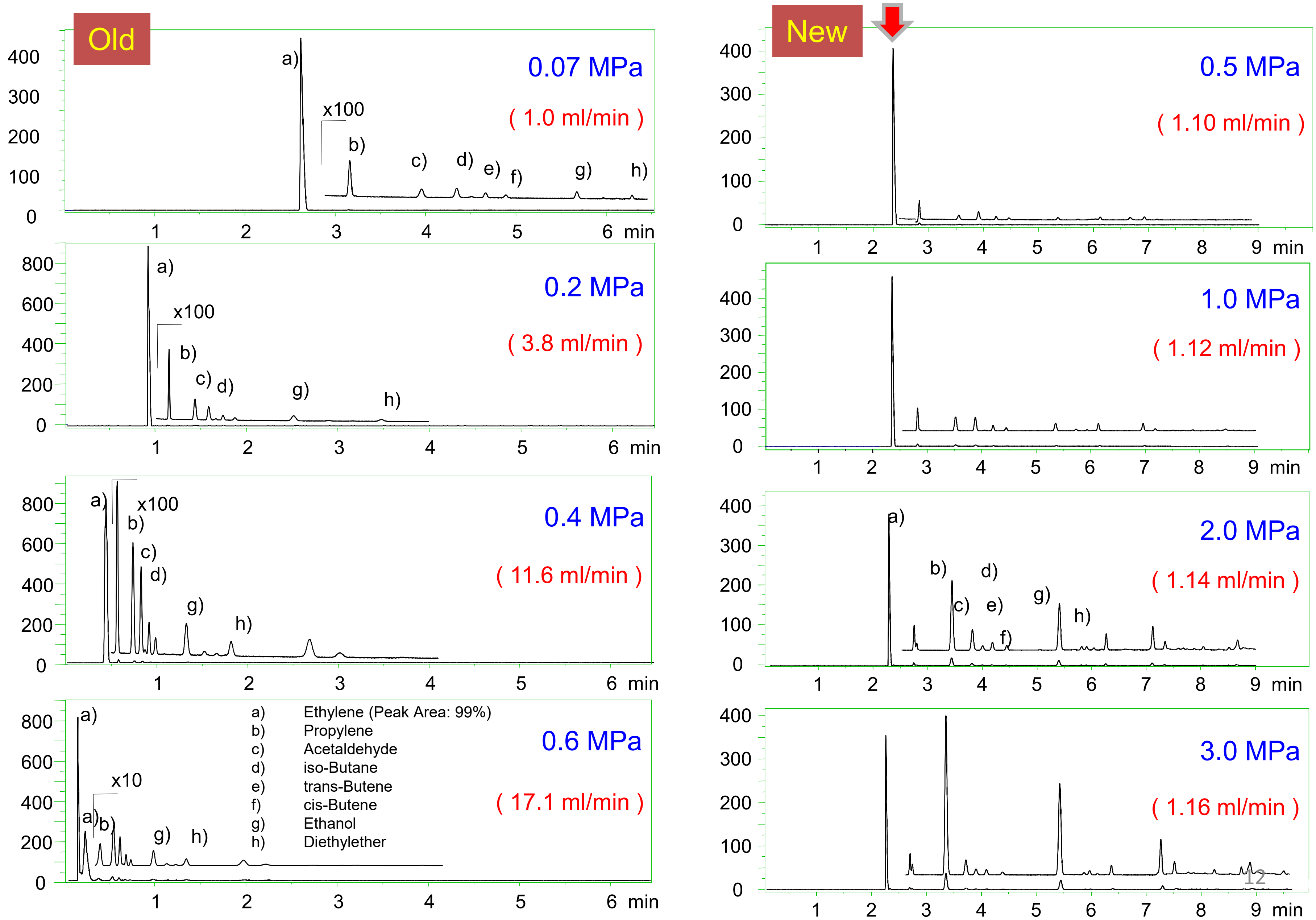
OPTION
HP flow module



FRONTIER LAB

No retention time shift due to BP regulators and open split interface

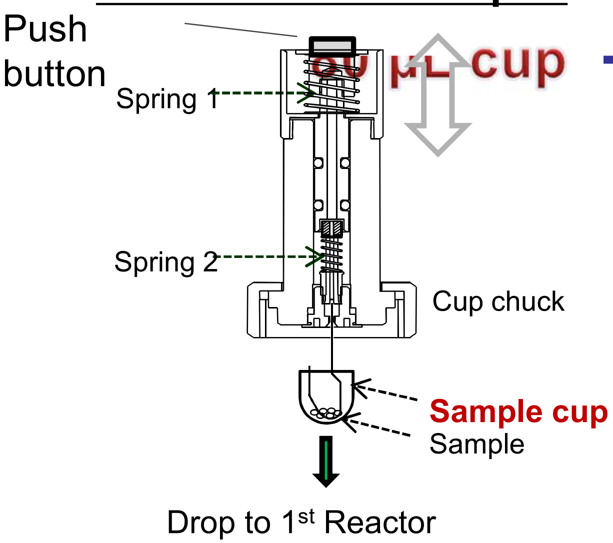
Catalyst (ZSM-5) at 230ºC, : BP1: 0.5-3.0 MPa, BP2: 0.1 MPa, Restrictor: 40 cm , i.d. 50 μm, Column: UA1-30M-2.0F, Detector: FID

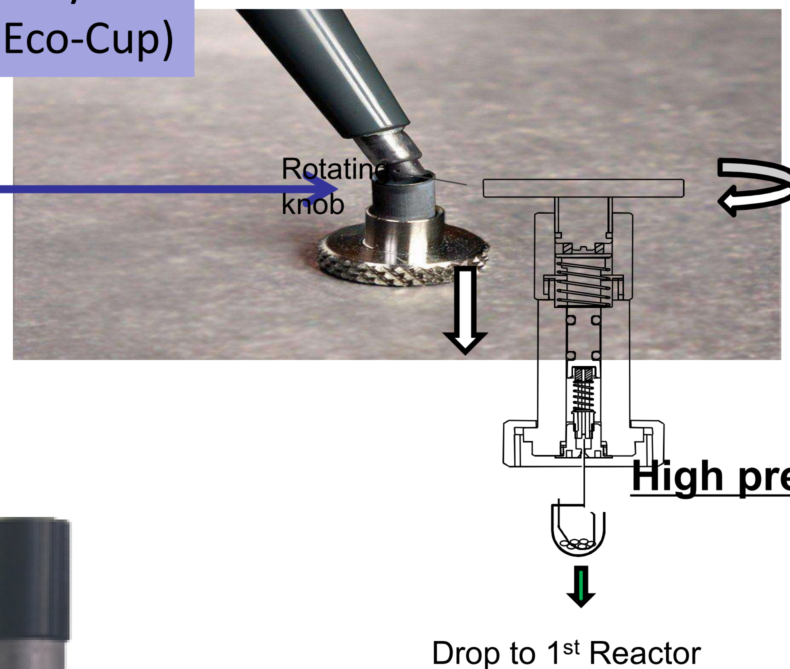


High pressure sample injection of solids

Sample is placed directly into the sample cup (Eco-Cup)

Standard solid sampler





High pressure solid sampler

FRONTIER LAB

Two applications using the high pressure Tandem µ-Reactor

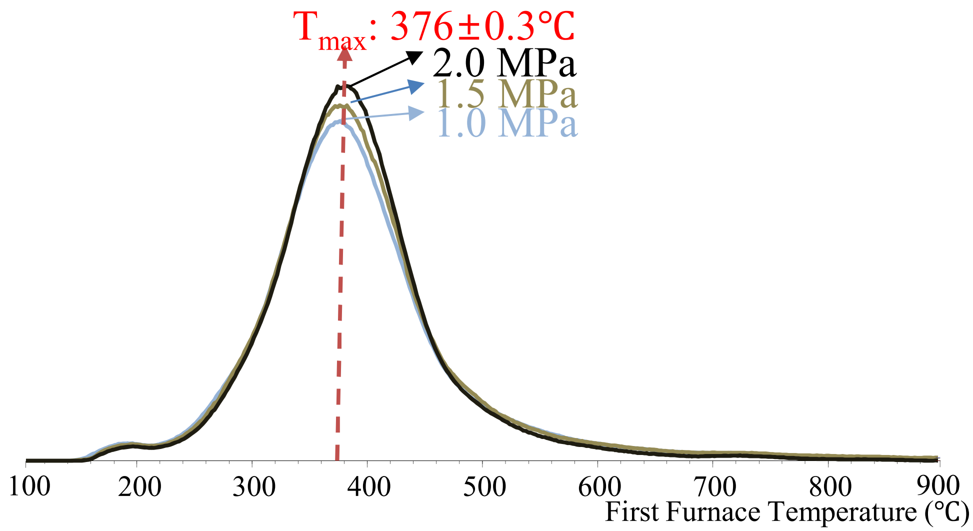
1. Conversion of lignin (He/H_2 and P)
2. Conversion of Ethanol (T and P)

Applying different parameters:

- ❖ Biomass (nature, amount)
- ❖ Catalysts (type, particle size, catalyst/biomass ratio)
- ❖ Temperature (1st and 2nd Reactor)
- ❖ Reaction-/Carrier-Gases (He/H_2)
- ❖ (High)-Pressure
- ❖ GC/MS settings

FRONTIER LAB

Non-catalytic pyrolysis of kraft lignin under high pressure helium (carrier gas)

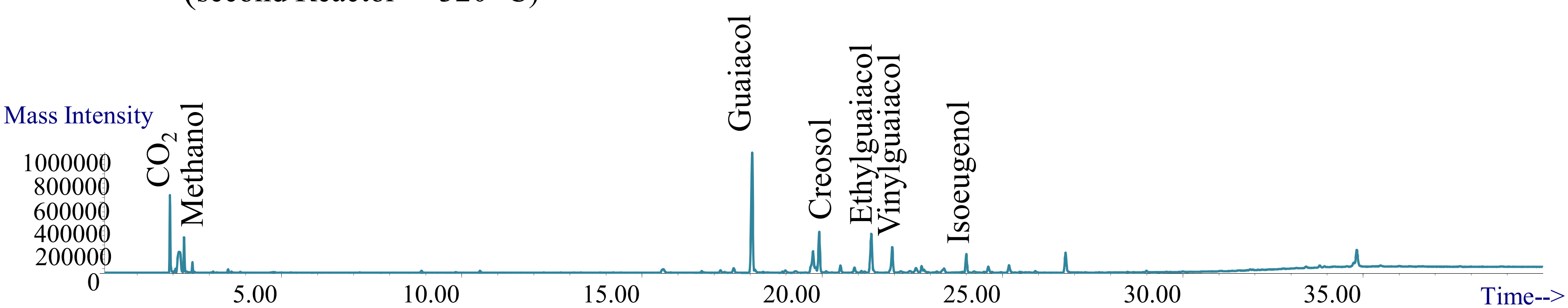


EGA Thermogram of Kraft Lignin

(second Reactor = 320 ^{0}C)

Remained char after EGA-MS analysis

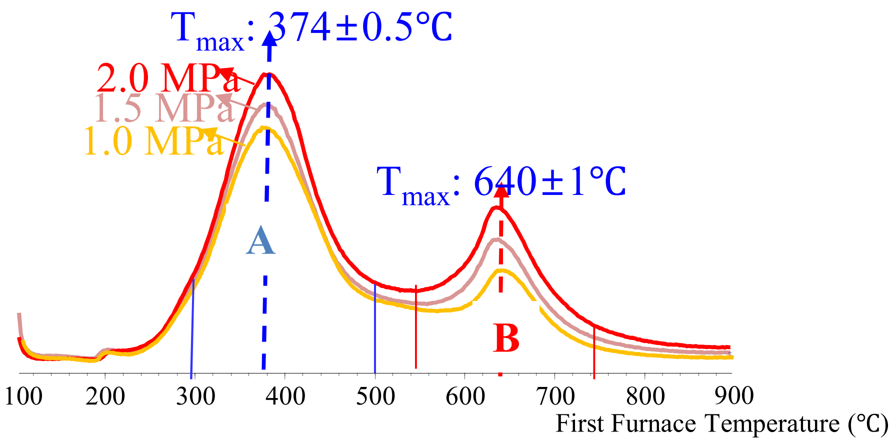
Pressure (MPa)	1.0	1.5	2.0
Char (wt.%)	44.5	44.2	45.3



Pyrogram obtained heart-cut EGA-GC/MS analysis from 300 to 500°C under 2MPa of helium atmosphere

FRONTIER LAB

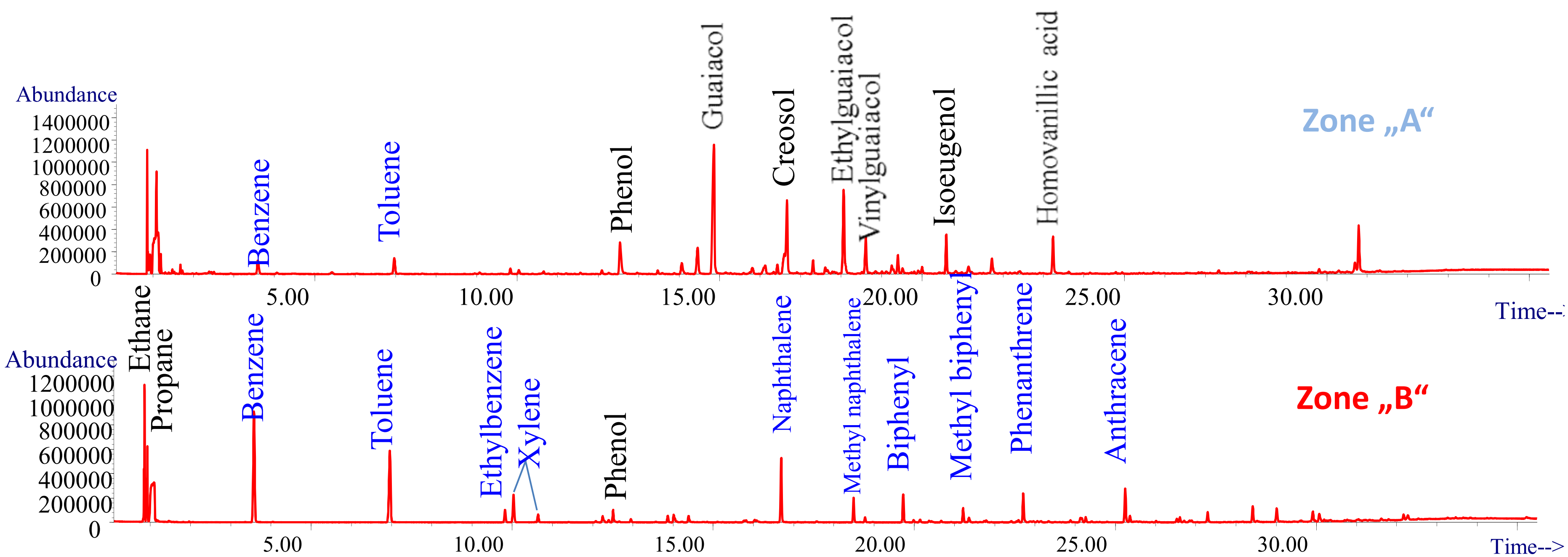
Non-catalytic „hydropyrolysis“ of kraft lignin under high pressure hydrogen



EGA Thermogram of Kraft Lignin under Different Hydrogen Pressure.

Remained char after EGA-MS analysis

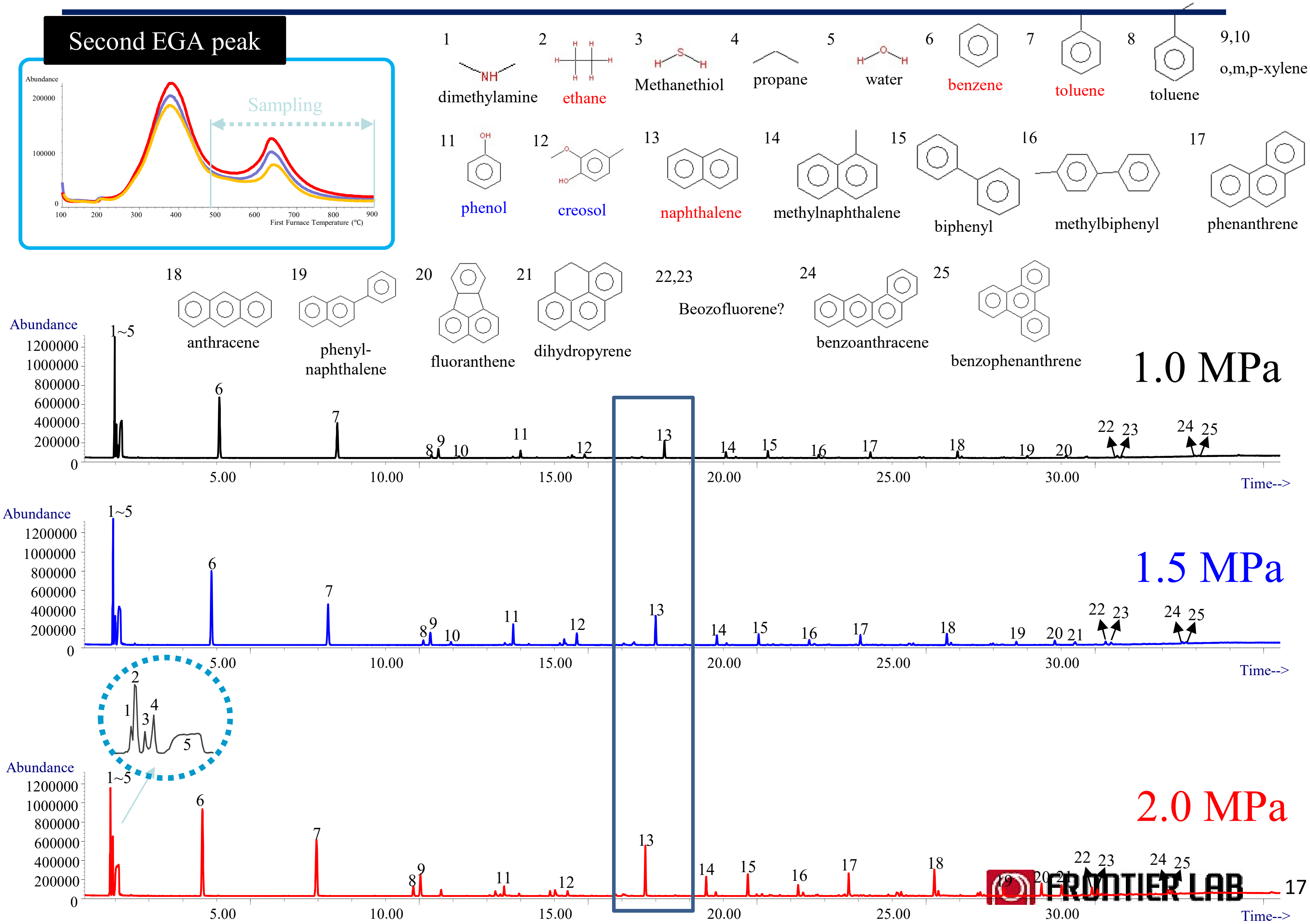
Pressure (MPa)	1.0	1.5	2.0
Char (wt.%)	35.2	26.3	21.4



Pyrogram obtained heart-cut EGA-GC/MS analysis from 100 to 800 ^{0}C under 2MPa of hydrogen atmosphere

FRONTIER LAB

Heart-Cut EGA-GC/MS at Different Hydrogen Pressures



Results lignin conversion under high presssure hydrogen

- Heart-Cut EGA-GC/MS results showed that most of pyrolyzates of first EGA peak were phenolic pyrolyzates of lignin, such as guaiacols, pyrocatechol, cresol, eugenol, and homovanillic acid.

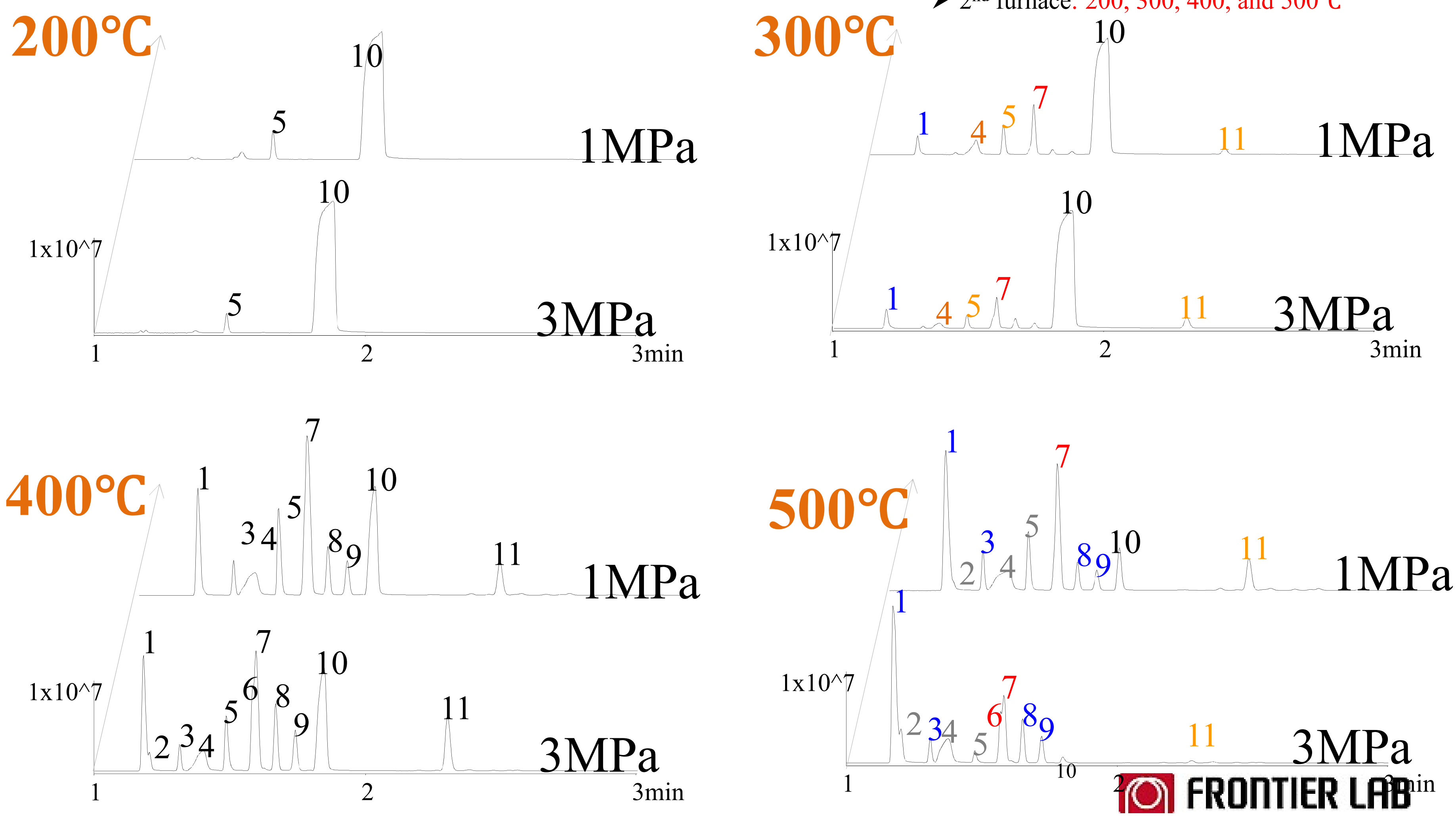
- Second EGA peak shows quite large amount of valuable aromatic compounds such as BTEXs, naphthalenes, biphenyls, phenanthrenes, and anthracenes and their peak intensities were increased under higher pressure. This can indicated that there is an important interaction between char intermediates and hydrogen gas and this interaction can produce large amount of aromatic oil under high hydrogen pressure.

FRONTIER LAB

Ethanol over MgO-SiO2 Catalyst under hydrogen and high pressure plus different catalytic bed temperatures

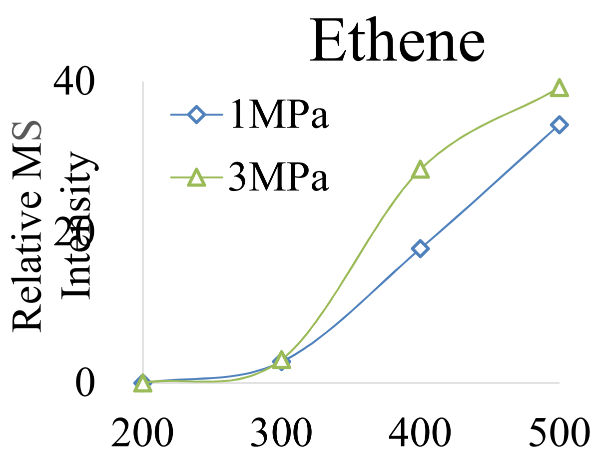
1: Ethylene, 2: Ethane, 3: Propene, 4: Water, 5: Acetaldehyde, 6,8,9: Butene, 7: Butadiene, 10: Ethanol, 11: Diethyl ether

- 1st furnace: 300°C
- 2nd furnace: 200, 300, 400, and 500°C

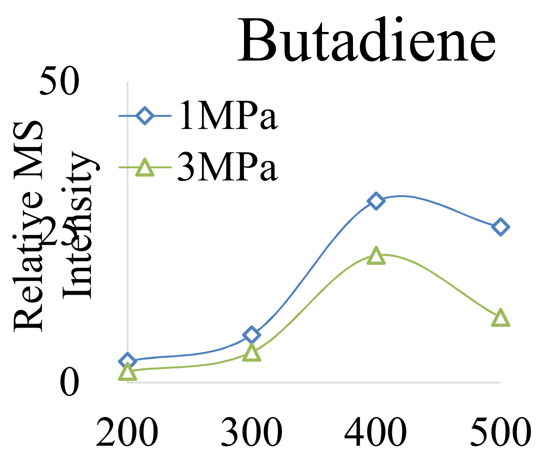


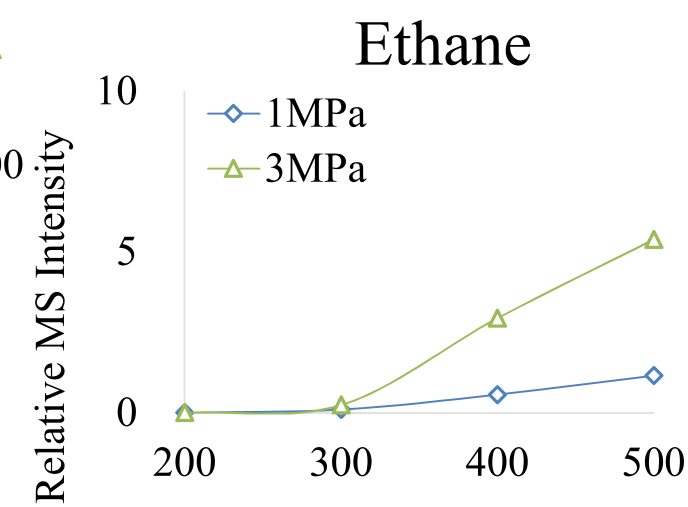
FRONTIER LAB

Ethanol over MgO-SiO2 Catalyst under hydrogen and high pressure:
Different catalytic bed temperatures



- *Ethanol conversion and product distribution were quite different at different catalyst bed temperature.*
- *Butadiene and ethene yield were maximized at 400 and 500 ℃, respectively.*
- *By increasing reaction pressure from 1 to 3MPa, butadiene yield was decreased, however, ethene and ethane yields were increased at all applied temperatures*





Experimental Conditions

- Sample: Ethanol, 2ul
- Catalyst: $MgO-SiO_2$, 60mg
- 1st furnace: 300°C
- 2nd furnace: 200, 300, 400, and 500°C
- BP1: 1, 3 MPa
- BP2: 42 KPa (H_2)
- System Split ratio: He 500:1

FRONTIER LAB

SUMMARY

- Tandem µ-Reactor facilitates the rapid characterization of catalysts and biomasses
- Full spectrum of operating parameters can be investigated – SW controlled / online
- Easy and fast exchange of catalysts
- Real time analysis of gaseous or liquid samples
- automated analysis of solids (using "Autoshot" auto-sampler)
- species identification using MS
- High pressure option without loss of chrom. performance

The development and use of "best"/proper catalysts means new products, lower costs, and a broader range of feedstocks

FRONTIER LAB

Questions?

productivity
Renewable
Pt
olefinic
wood
Reactant gases
Tandem
SCREENING
micro
New
catalytic
GC/MS
Process
RAPID
catalyst
ISU
biomass
Reactor
H2O
GC/MS
ethylene
Carbon
FAST PYROLYSIS
Ru
New
saturated
Catalytic pyrolysis
Solids
engineer
FAST
Pd
New
Catalyst
Pilot Plant
Products
Rh
Scale-Up
Selective
High
RAPID
hydrogenation
Frontier Labs