Seminar

Use of micro-pyrolyzer-GC/MS for the polymer analysis and energy production

Hallym University
Young-Min, Kim.

Carrier

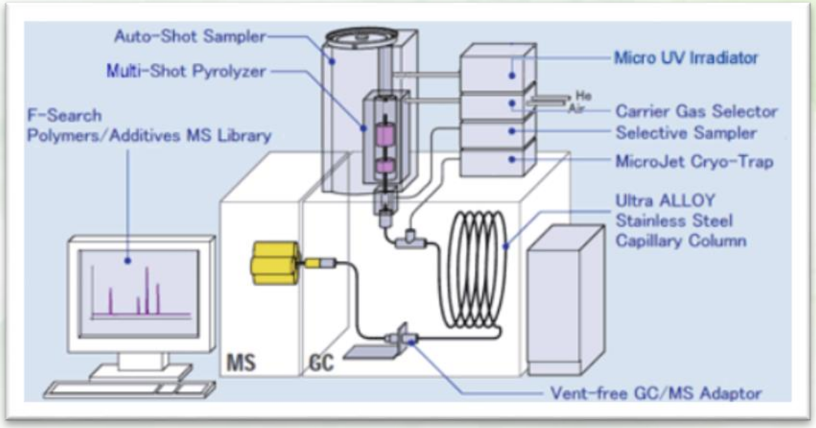
1. 1996.03~2005.08: B.A & M.D. at Hallym Univesity
2. 2005.09~2012.12: Young-In Scientific Co.
3. 2013.01~2013.12: National Forensic Service.
4. 2014.01~2014.12: Frontier Laboratories Japan, Japan R&D
5. 2010.03~2015.02: Ph.D. at University of Seoul
6. 2015.03~2016.02: Research Professor, Hallym University
7. 2016.02~: Associate Professor, Hallym University

Specialized in analytical pyrolysis technology!

1. First analytical instruments company in Korea

2. Small & Giant Company only for Pyrolyzer: Frontier-Lab Japan

Total Solution for Material Analysis



Tandem micro reactor

Pyrolyzer

UV-Irradiator

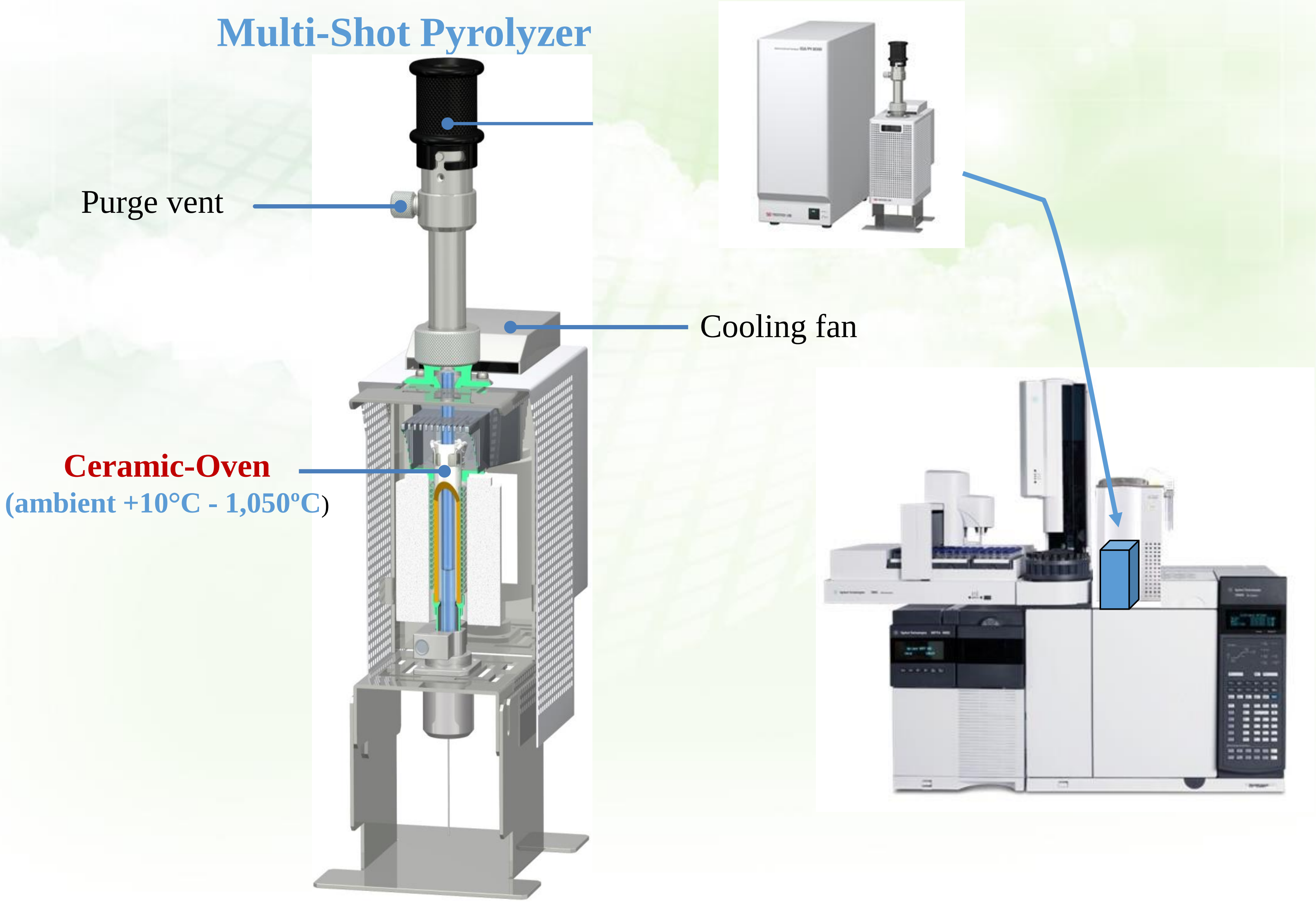
UA column

3. What is your choice for sample preparation

Matrix?

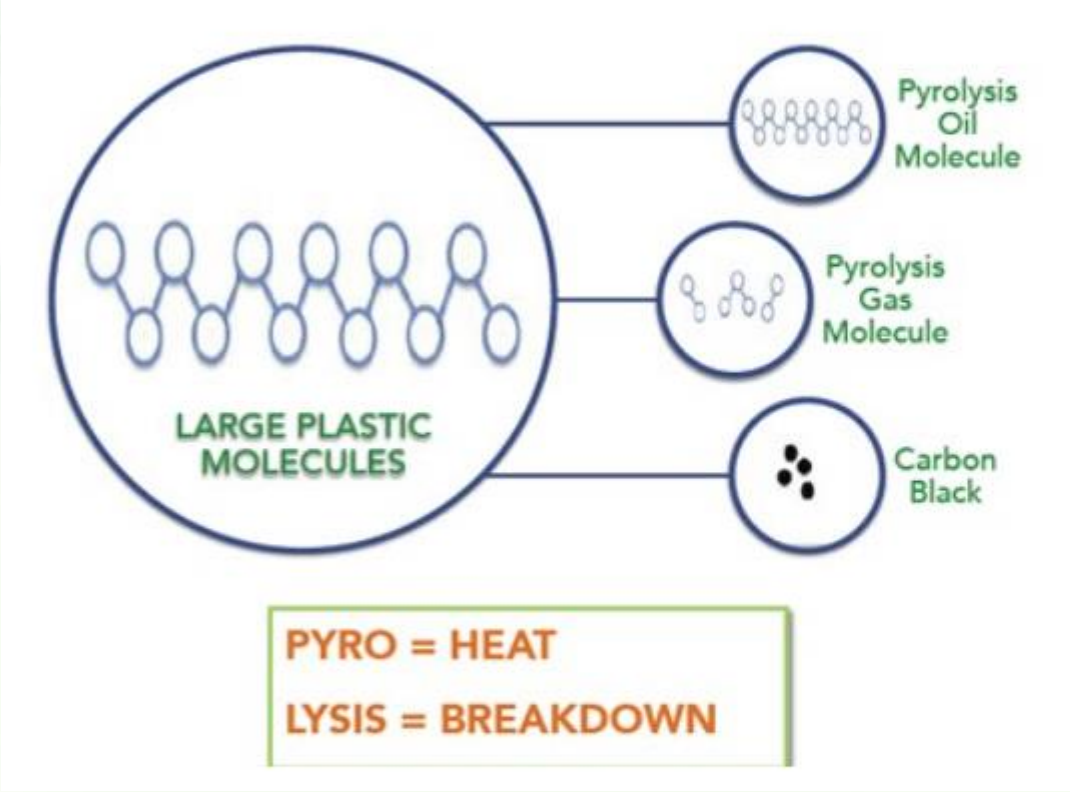
Target?

4. Pyrolyzer-GC/MS?



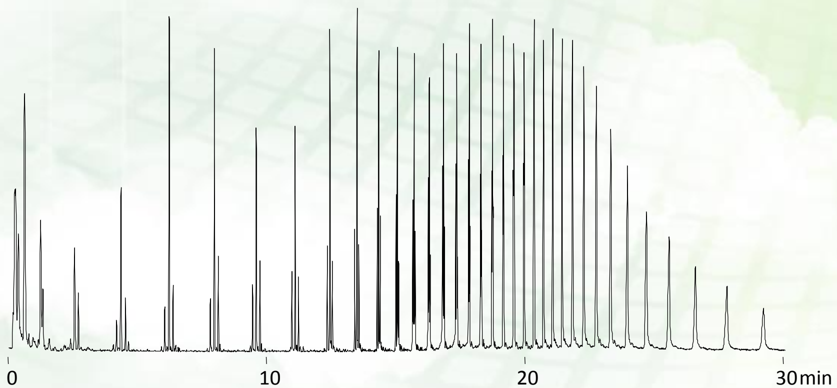
5. Pyrolysis

A thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen.

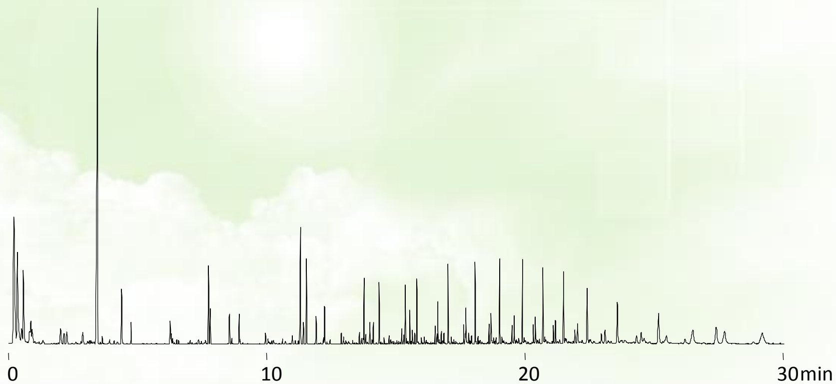


5.1. Finger Print Identification of Polymers by the pyrolyzates

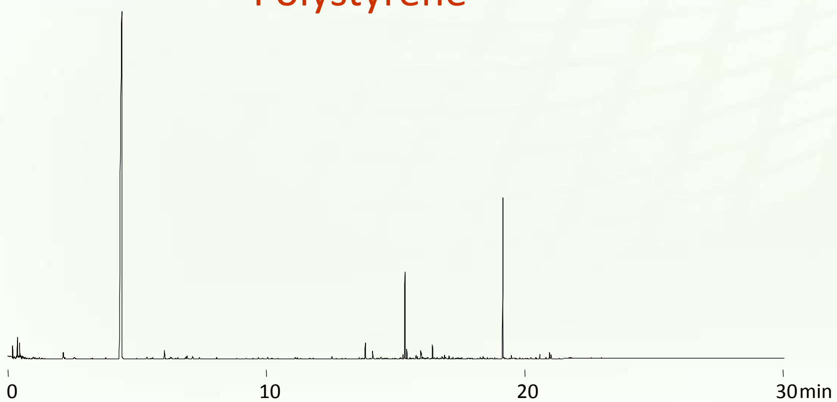
Polyethylene



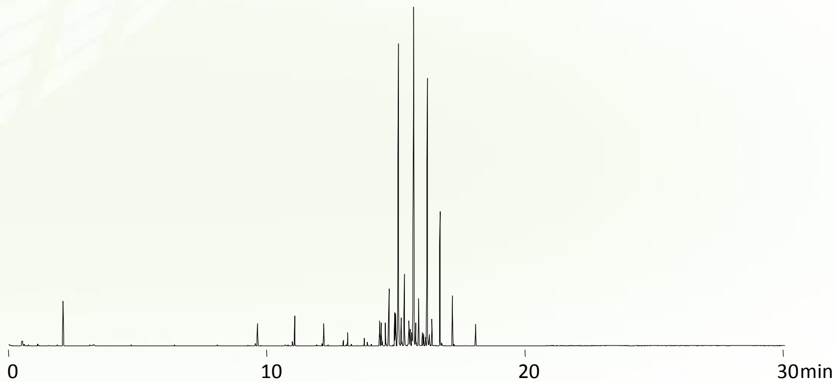
Polypropylene



Polystyrene



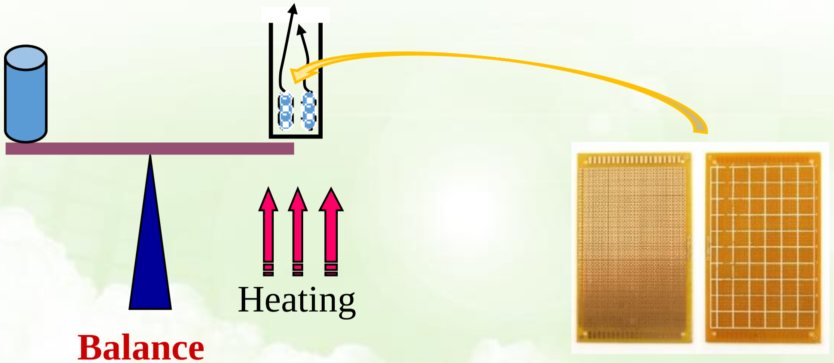
Acrylonitrile - methyl acrylate copolymer



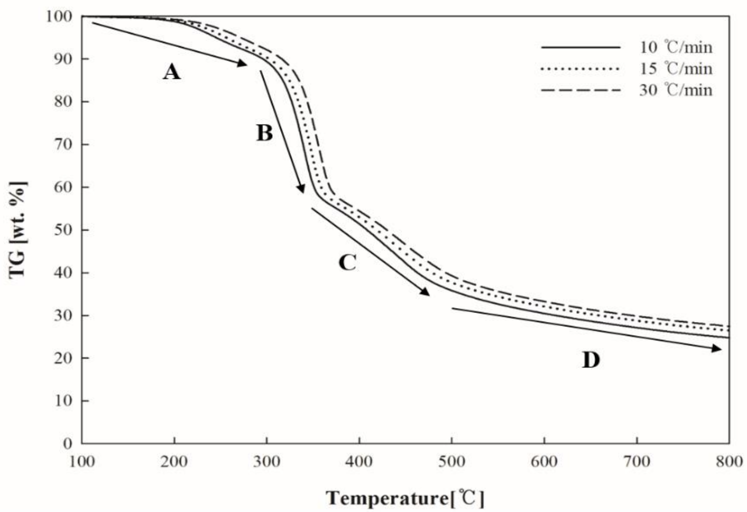
5. Other instrument for polymer analysis using Pyrolysis Technology

TGA

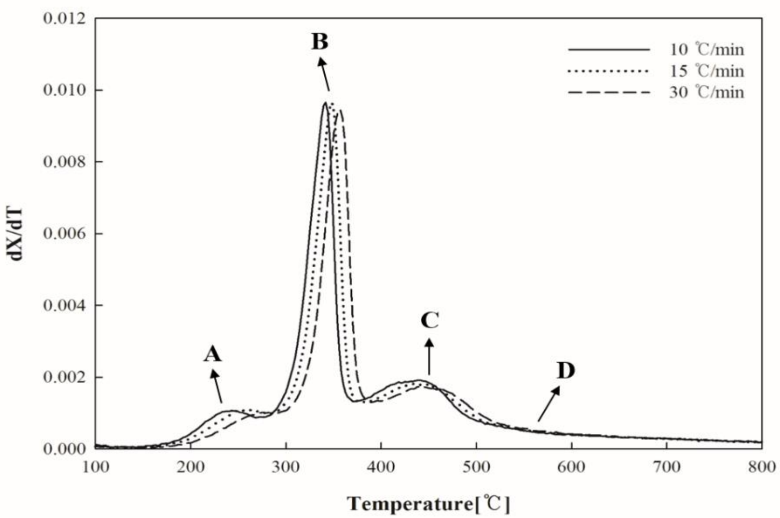
METTLER TOLEDO TGA2 model



<TG and DTG curves of paper laminated phenolic-printed circuit board>



(a) TG curves



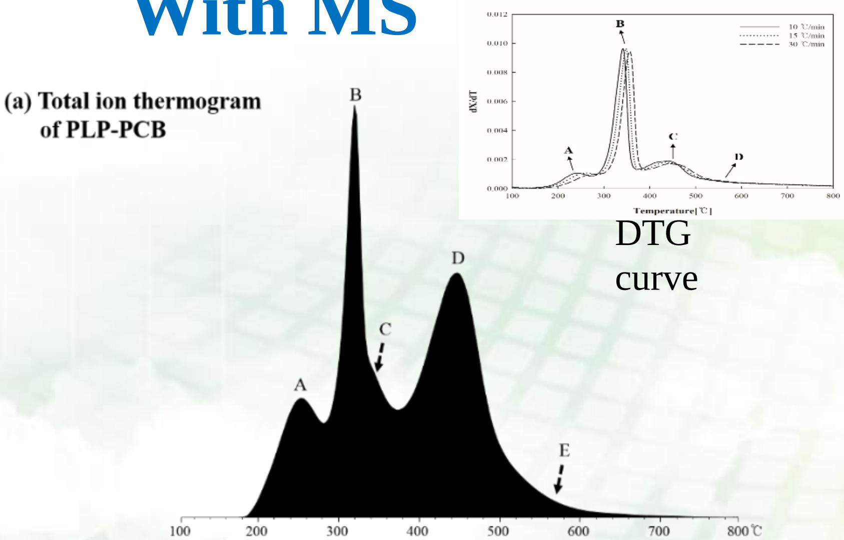
(b) DTG curves

1) Weight change as a function as temperature or time

2) Weight loss temperature by vaporization or decomposition

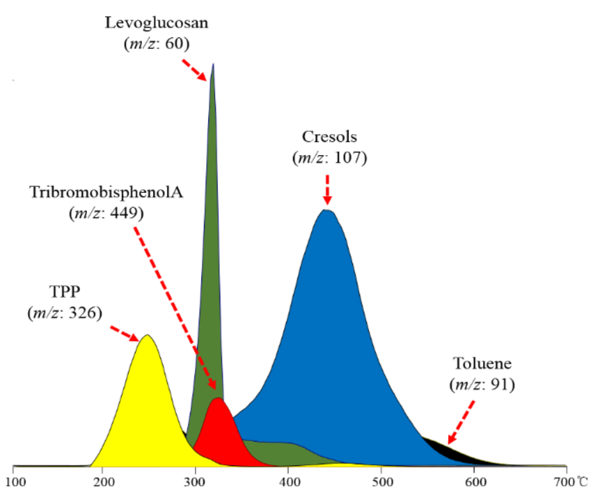
If MS is applied on pyrolysis technologies?

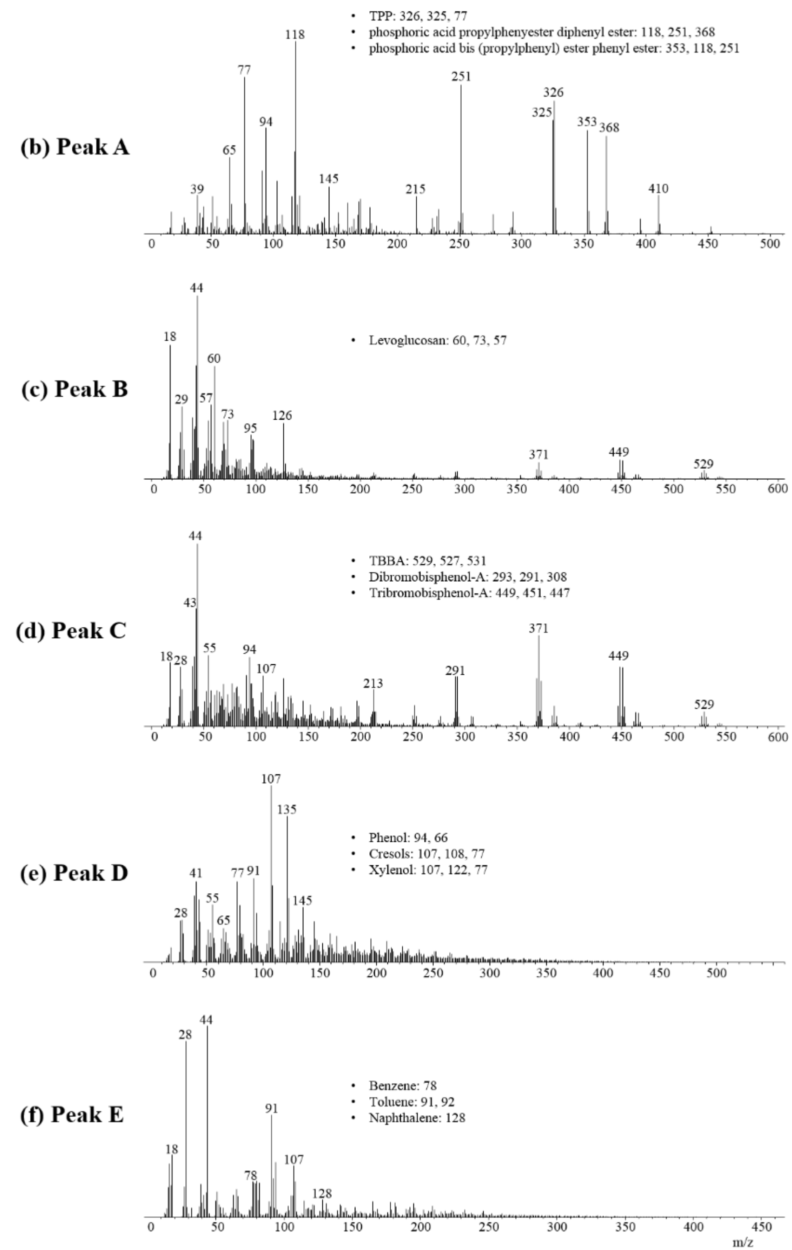
With MS



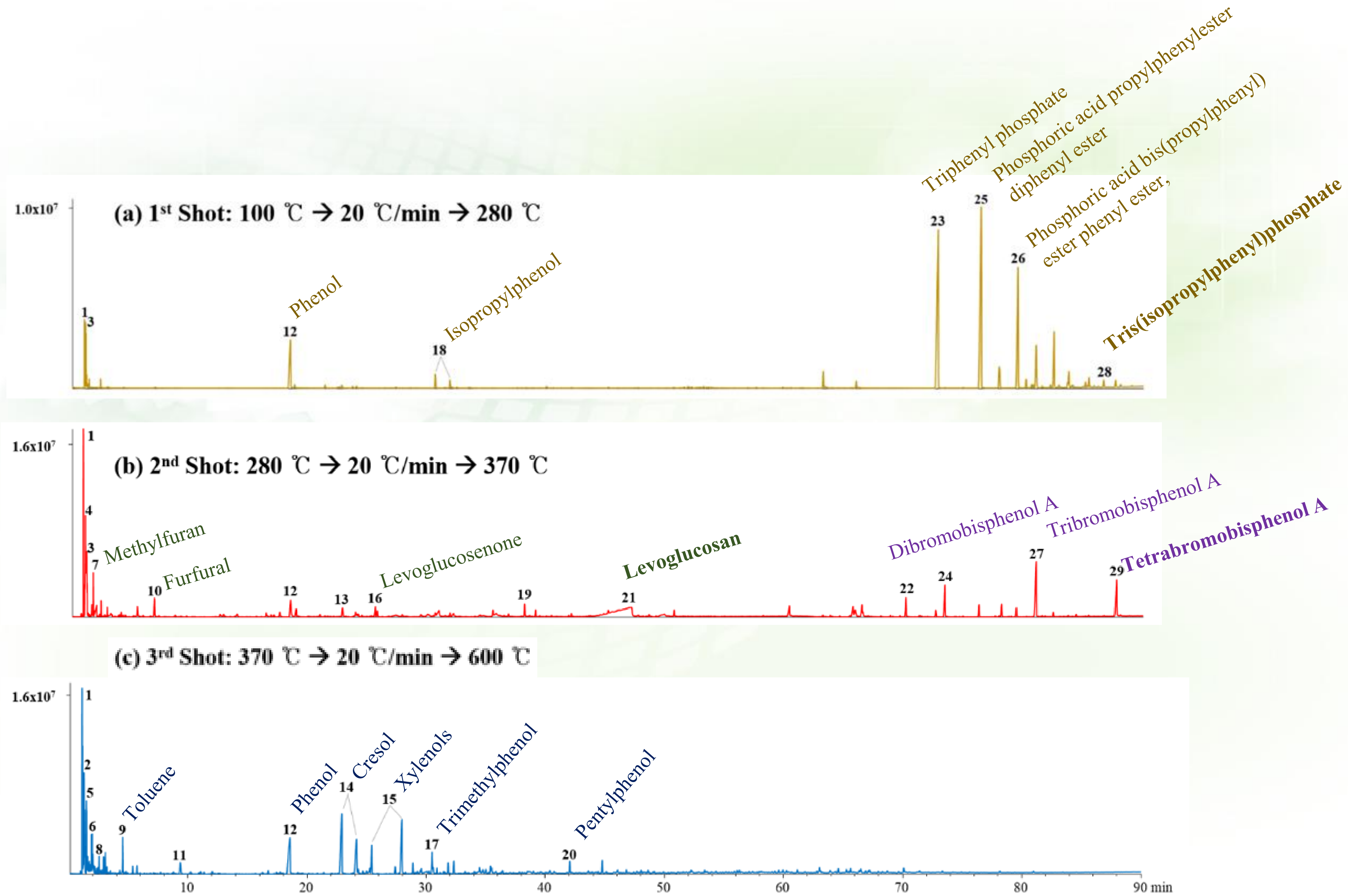
DTG curve

TG-MS curve (EGA-curve)

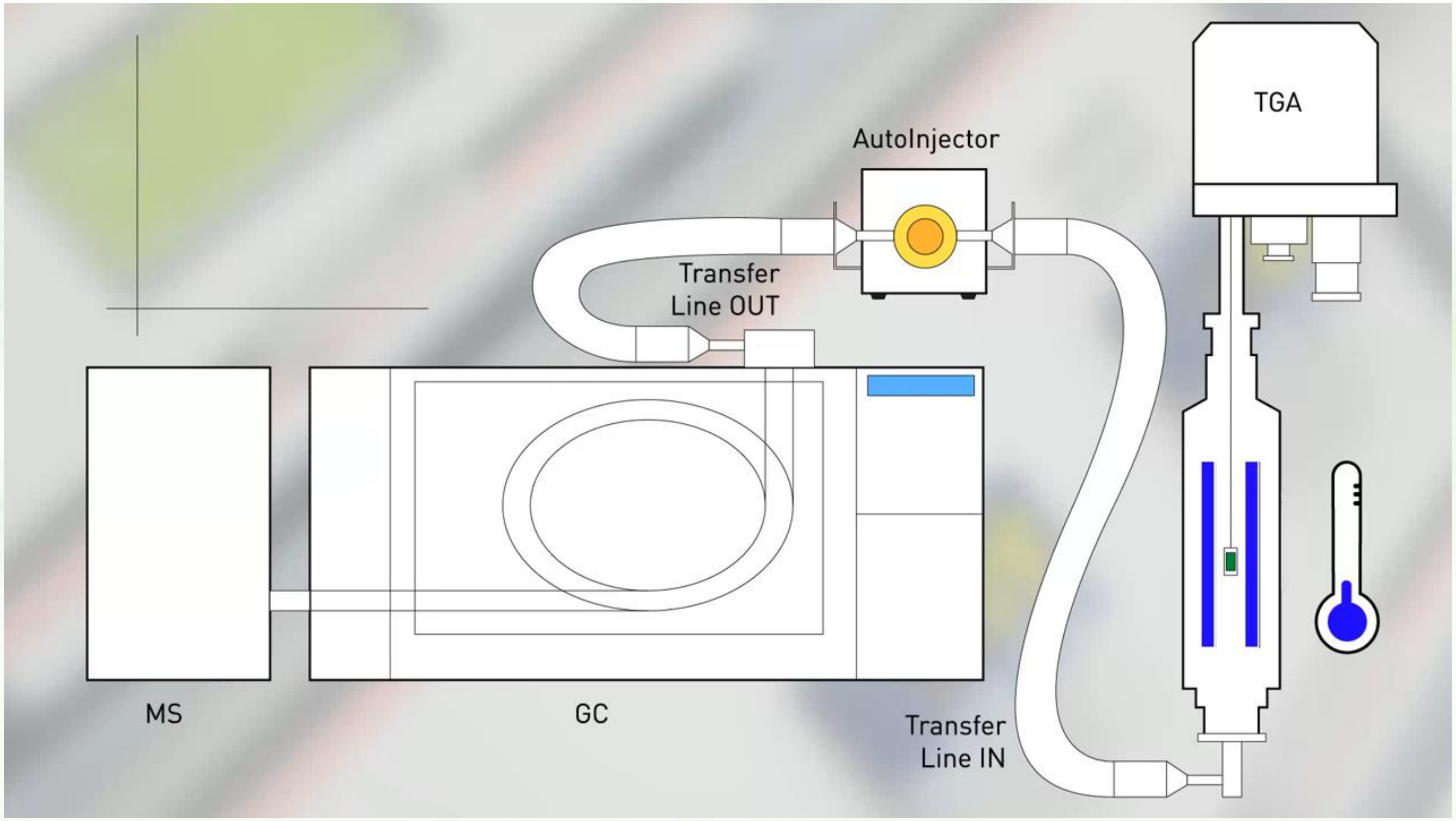




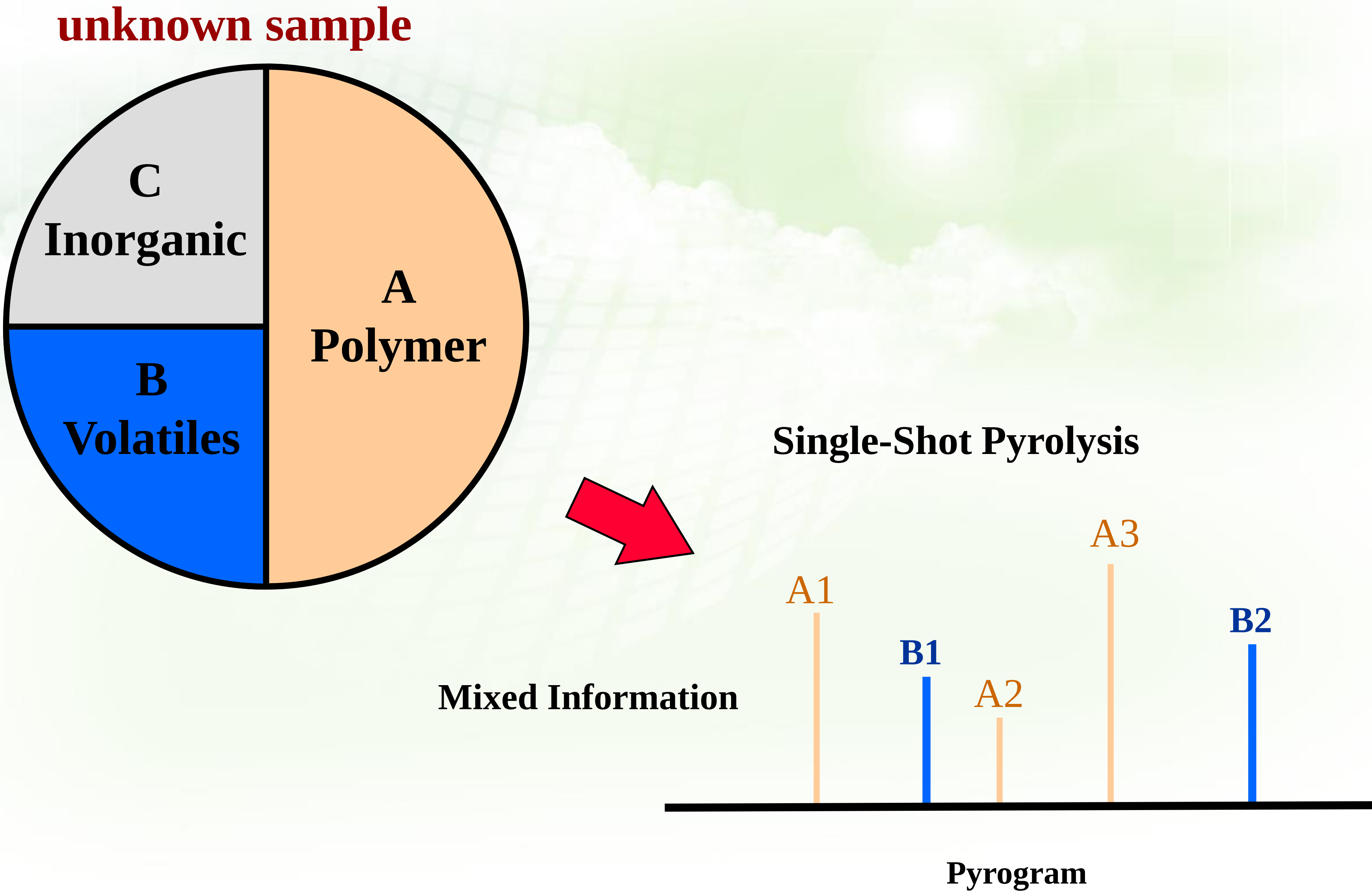
If GC/MS is applied on pyrolysis technologies?



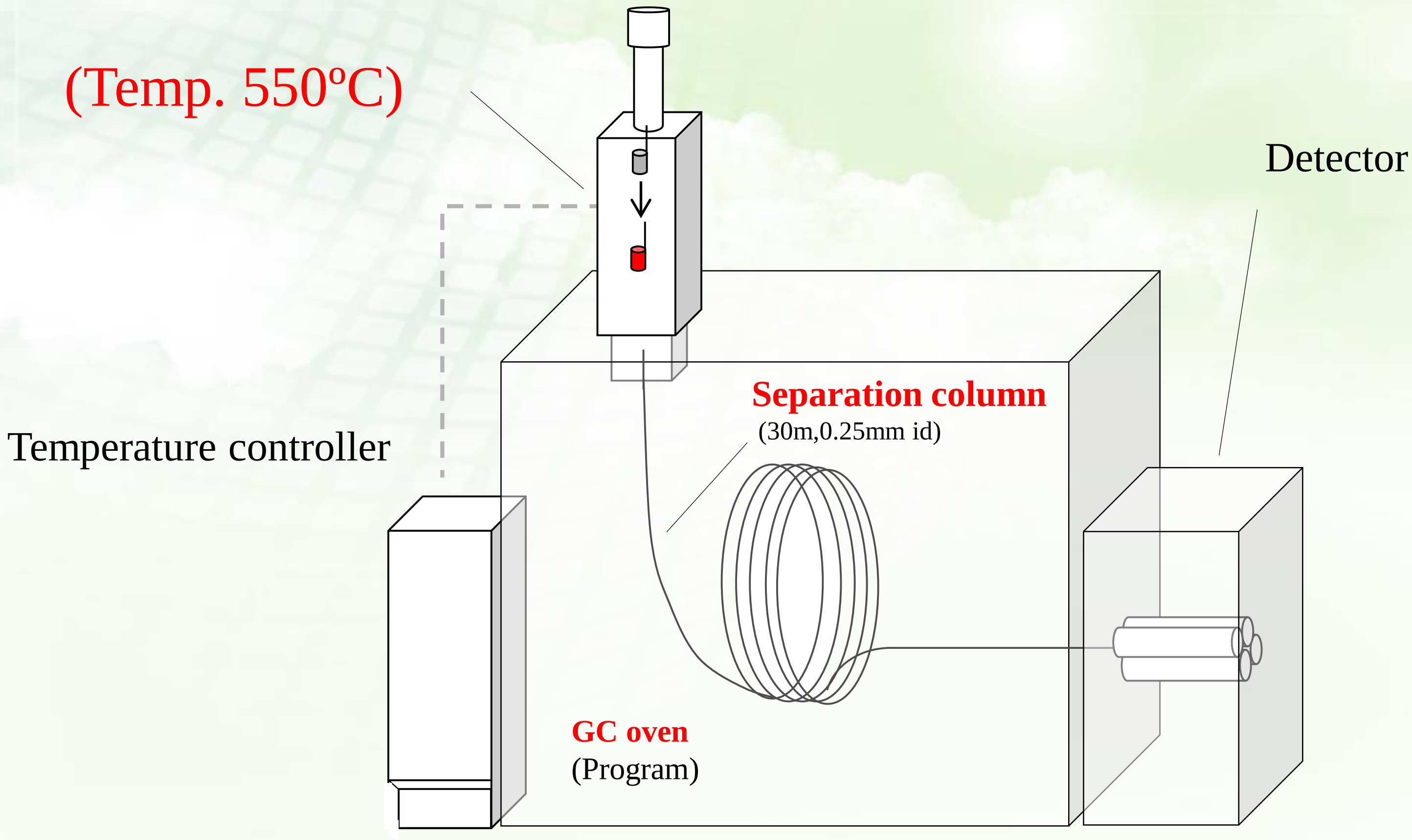
How TG-GC/MS works?



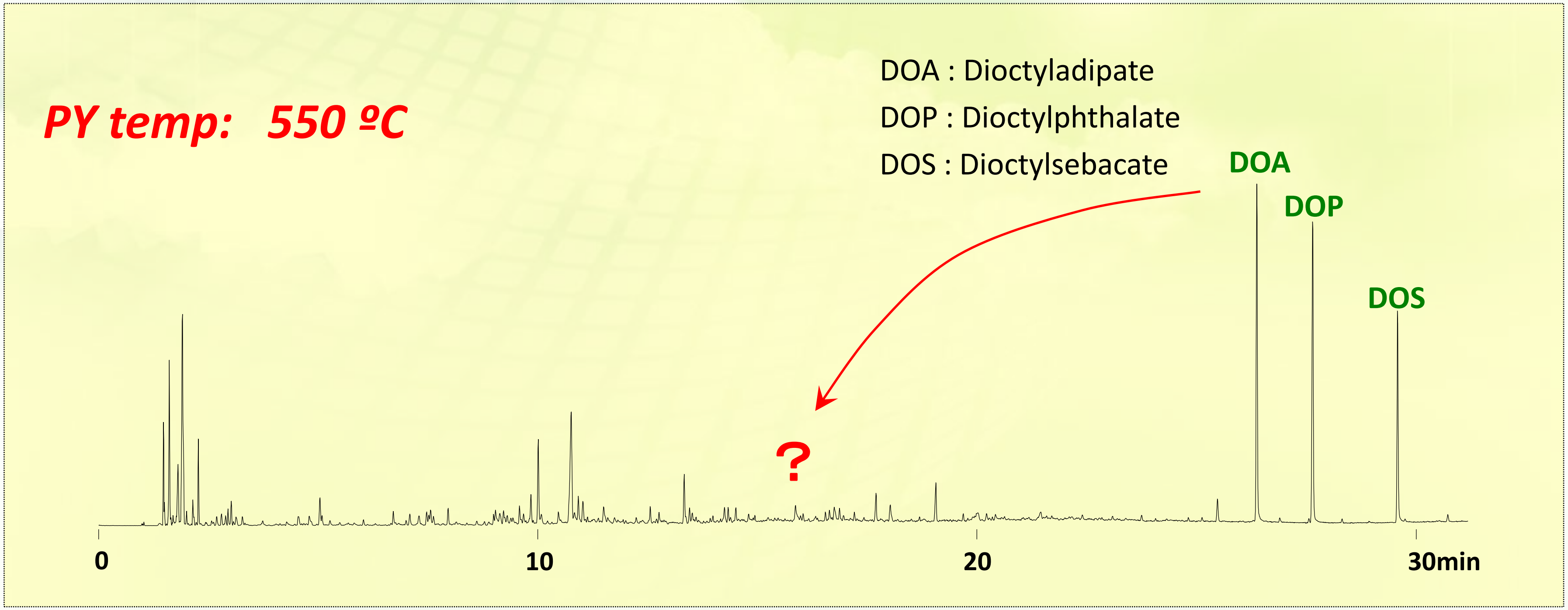
5.1. Analysis of Unknown Materials



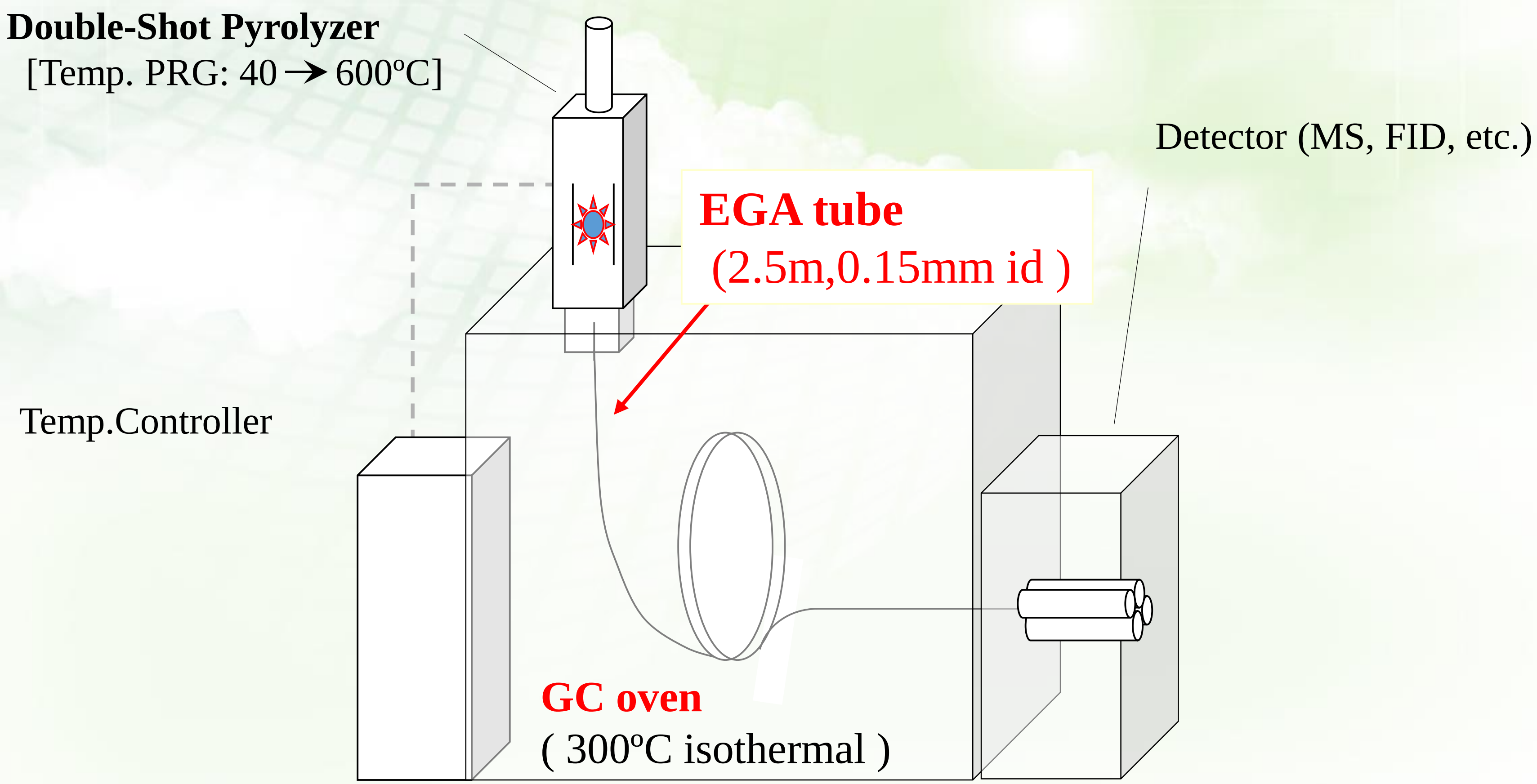
5.1. Single-Shot Flow Diagram



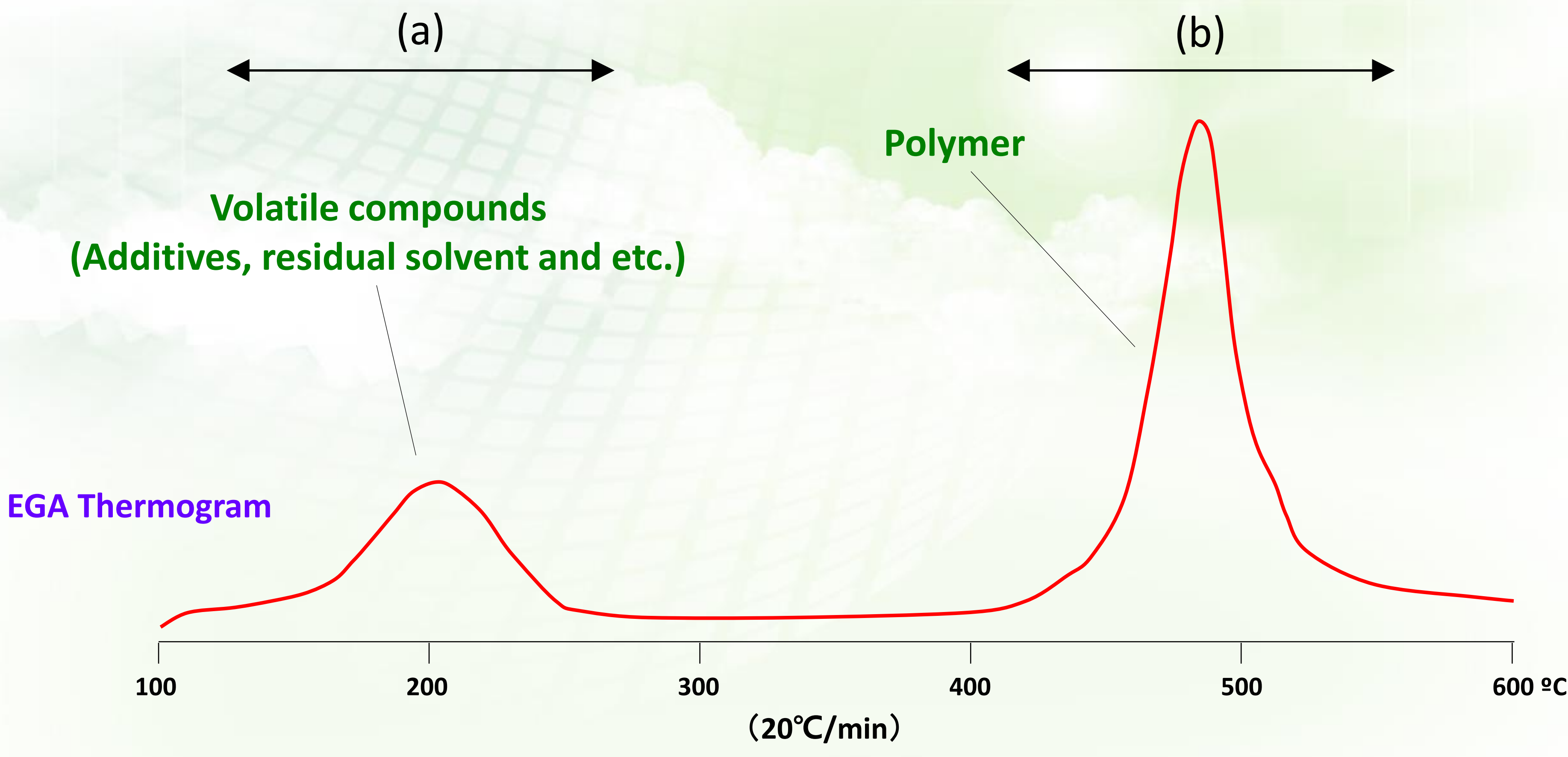
5.1. Single-Shot Flow Diagram



5.2. Evolved Gas Analysis-GC/MS



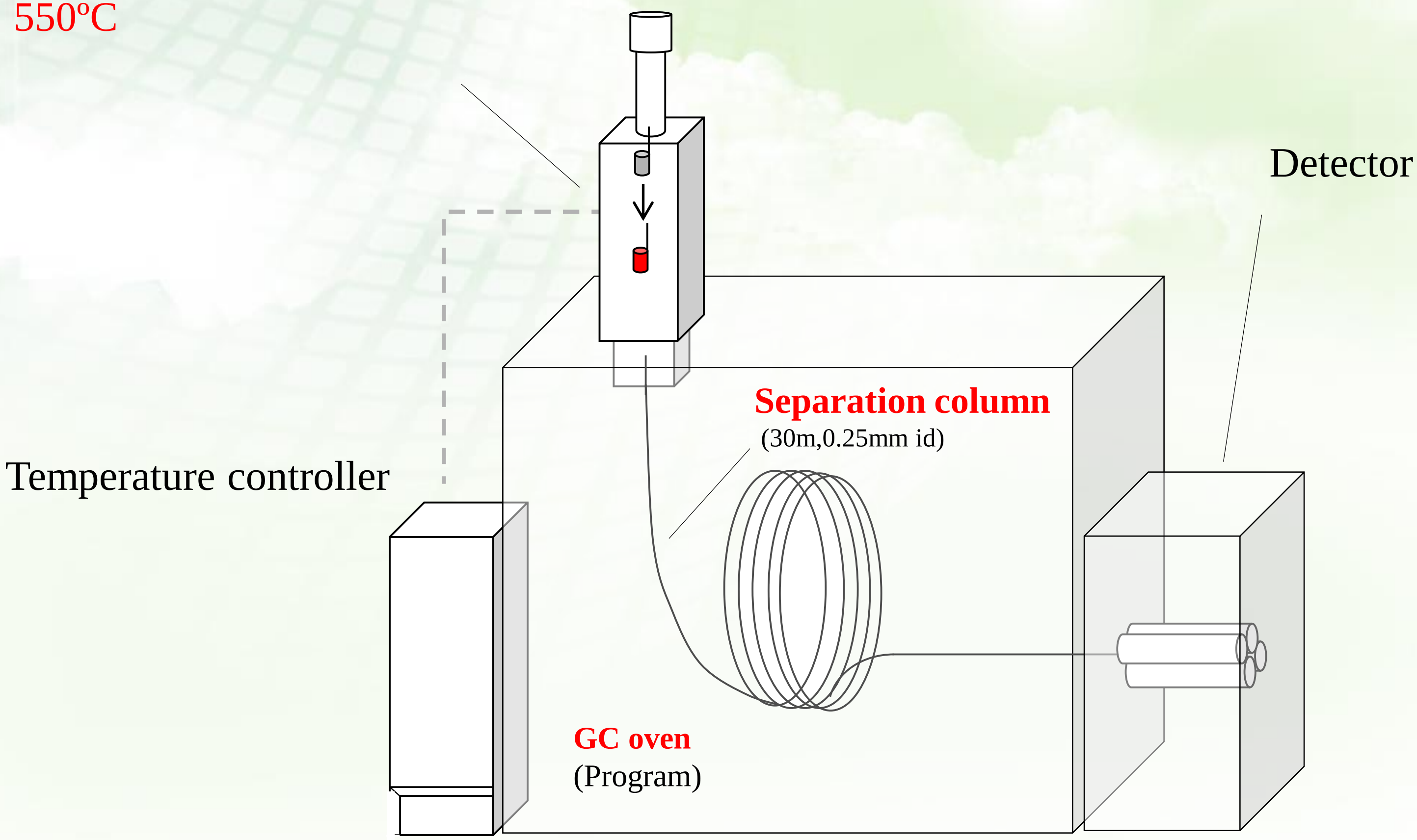
5.2. Evolved Gas Analysis-GC/MS



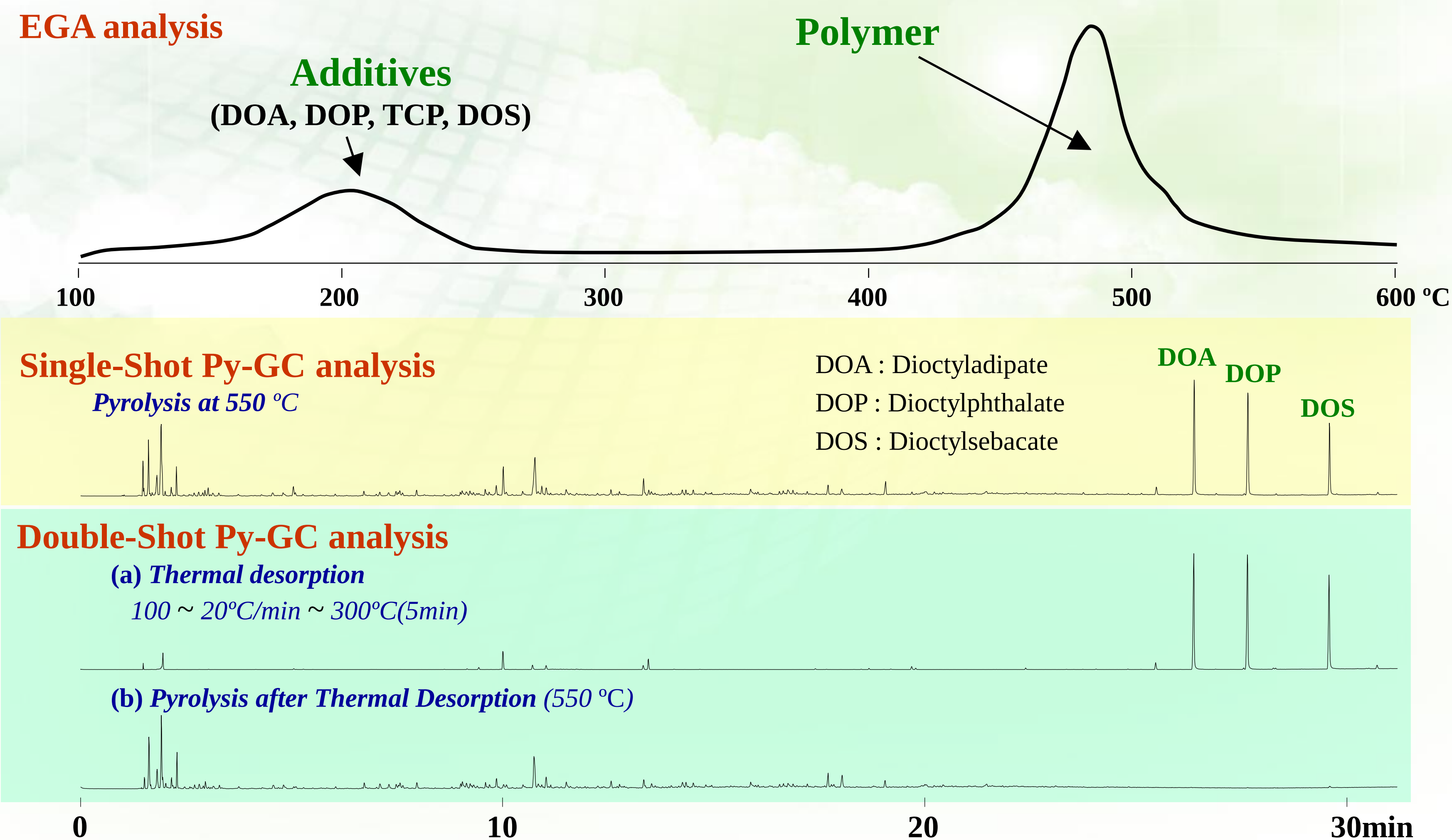
5.3. Multi-Shot Flow Diagram

Double-shot Pyrolyzer

Desorption :100→300ºC(20ºC/min, 5min hold)
Pyrolysis : 550ºC

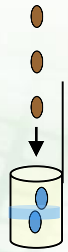


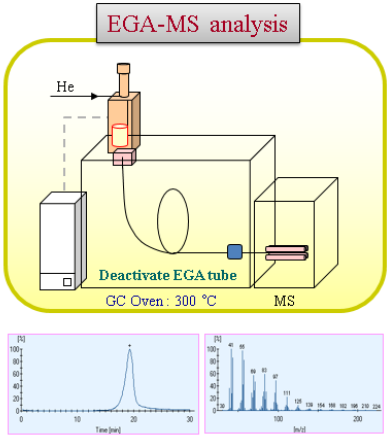
5.3. Analysis of NBR (acrylonitrile butadiene rubber) using EGA/ Single- & Double-Shot analysis

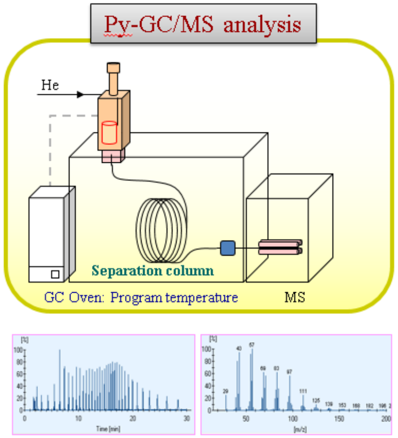


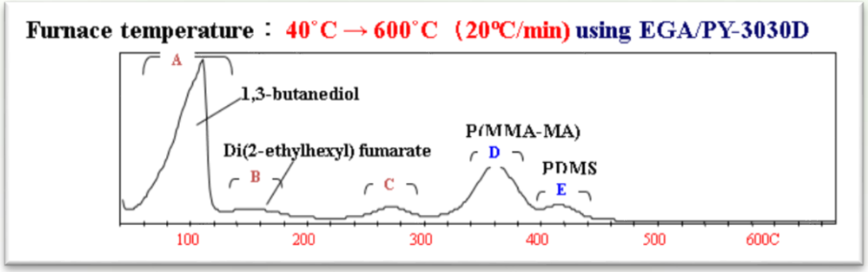
5.3. What is the organic composition of eyebrow?

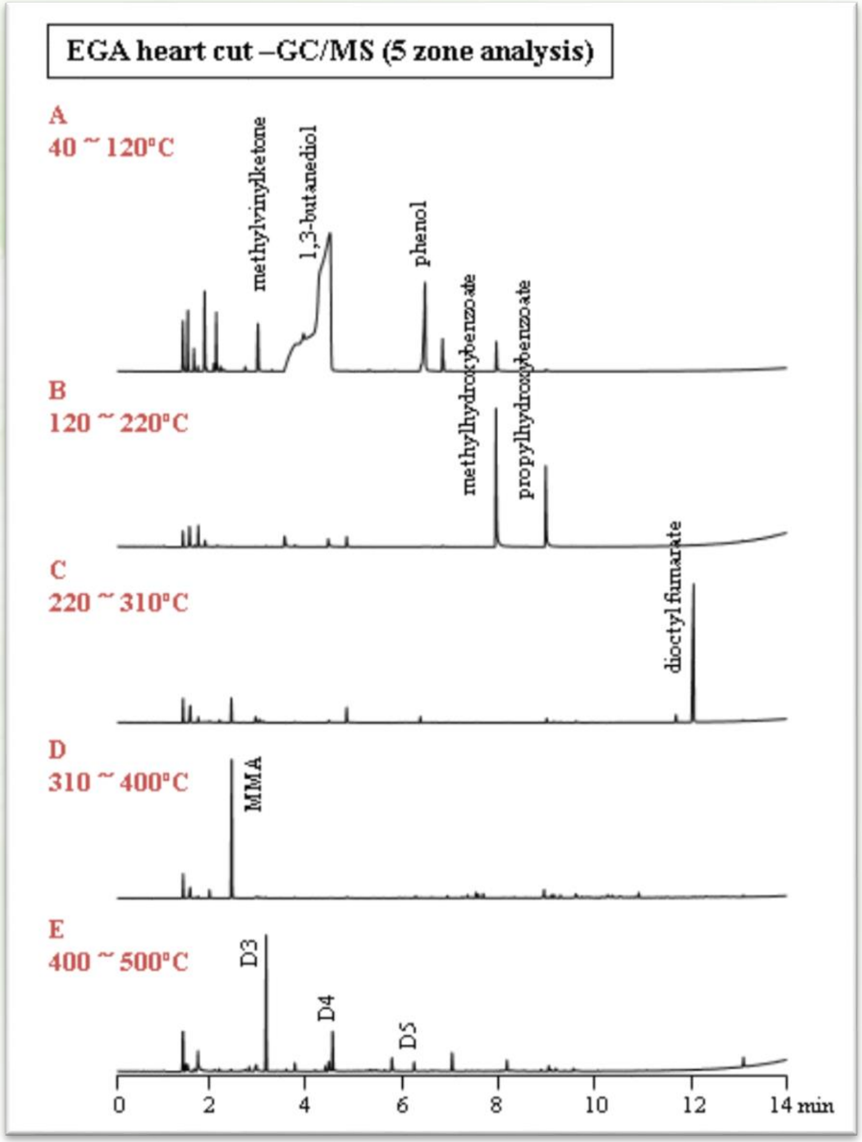
Eyebrow cosmetics
(TOMY TANAKA Co. Japan)



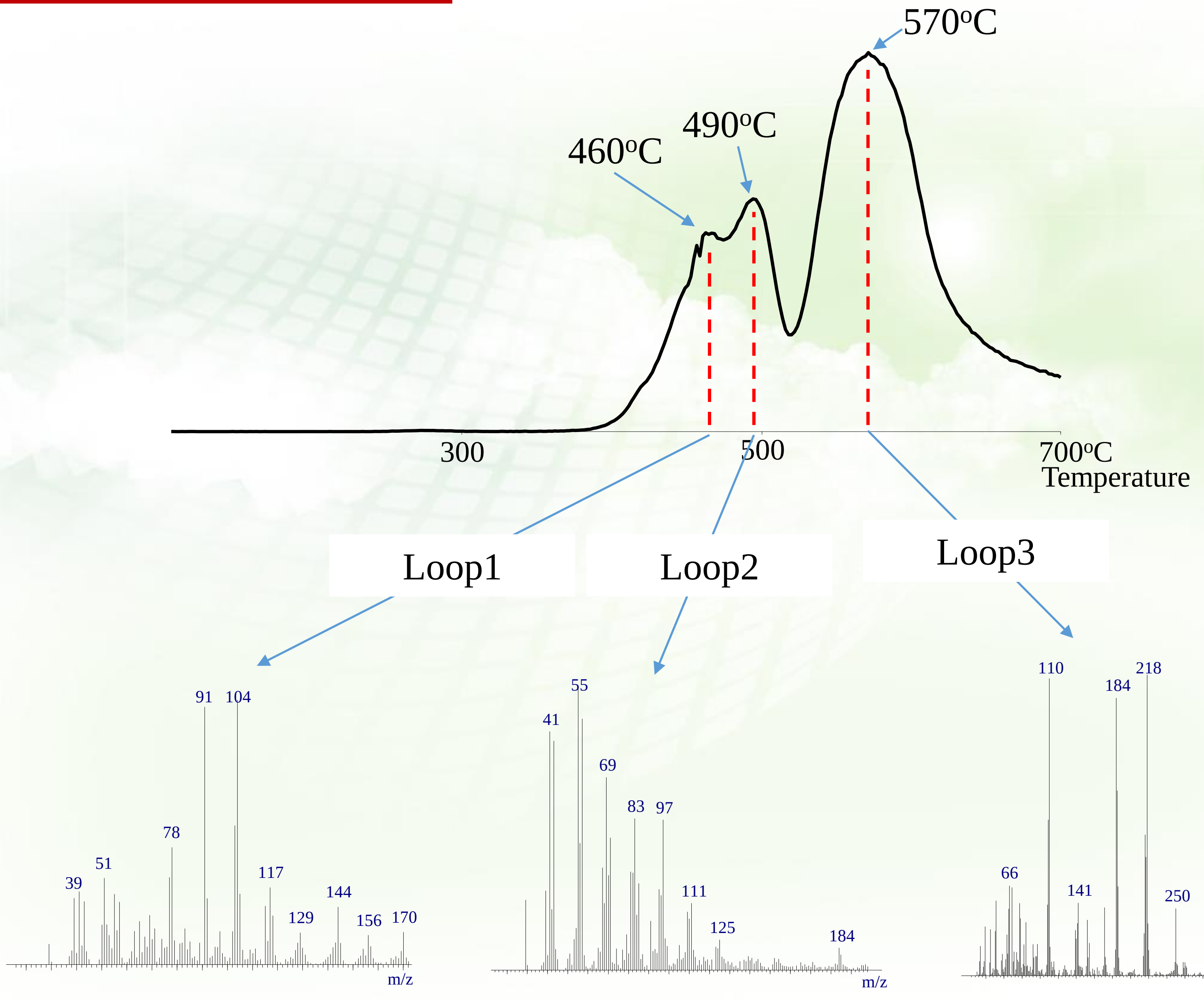




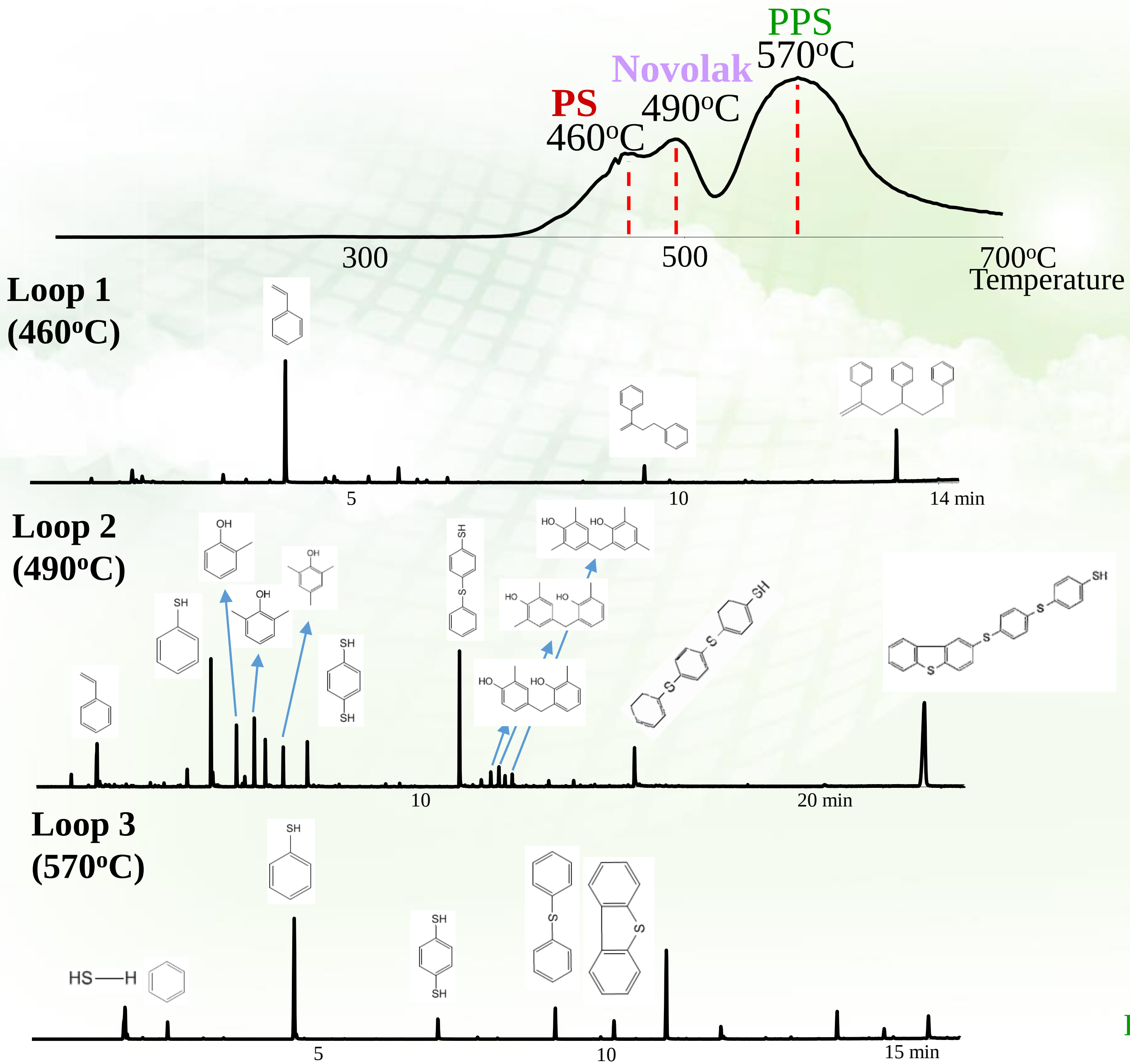




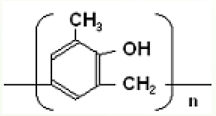
5.4. Analysis of brake pads for mobile vehicles



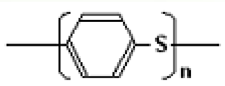
5.4. Analysis of brake pads for mobile vehicles



Polystyrene: PS



Cresol formaldehyde resin (Novolak)

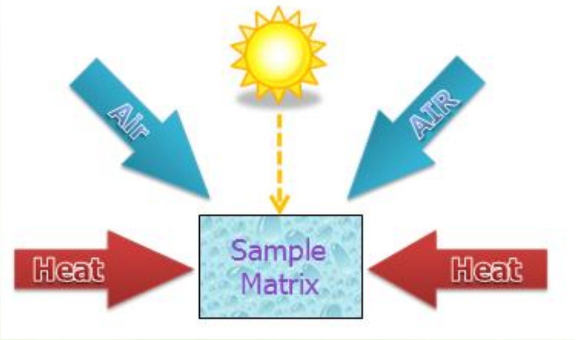


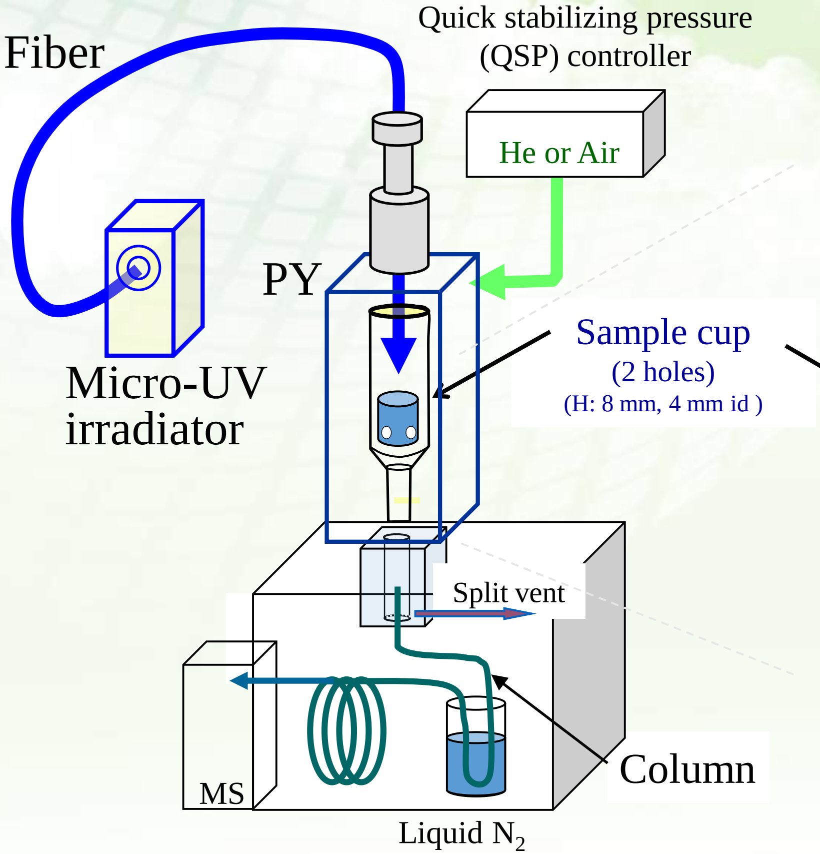
Poly(Phenylene sulfide):PPS

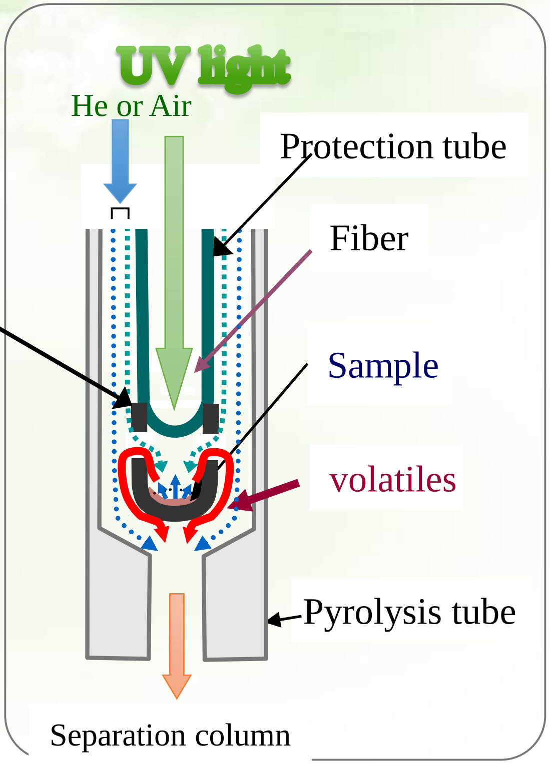
6. Polymer aging by UV ?

Aging Effect, UV-curing test, UV-Stabilizer test

1) Out Gas Analysis during UV-Irradiation
2) Aging Test (Weather O-meter plus TGA)



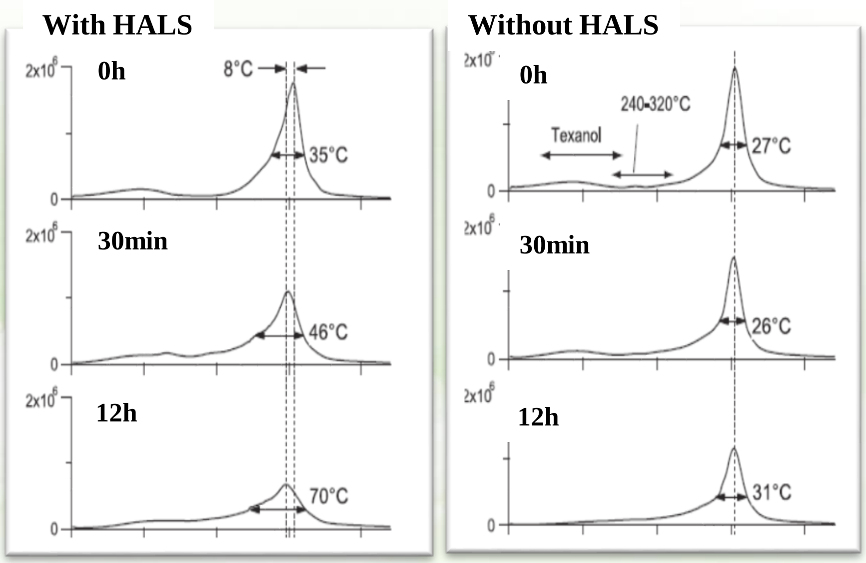




6.1. Why the color of paint was changed?

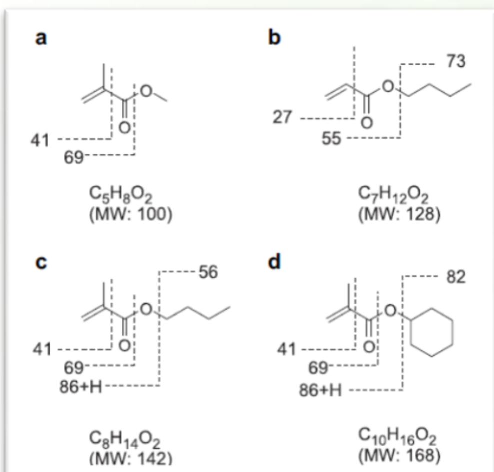
Deterioration of resin by UV (Polycarbonate)

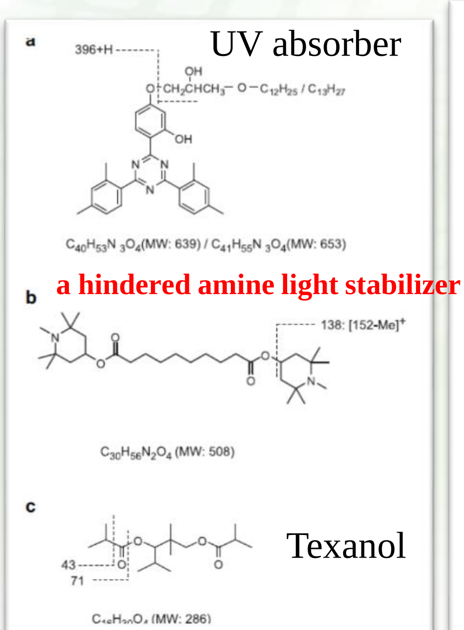
0h 30 min 12 hours

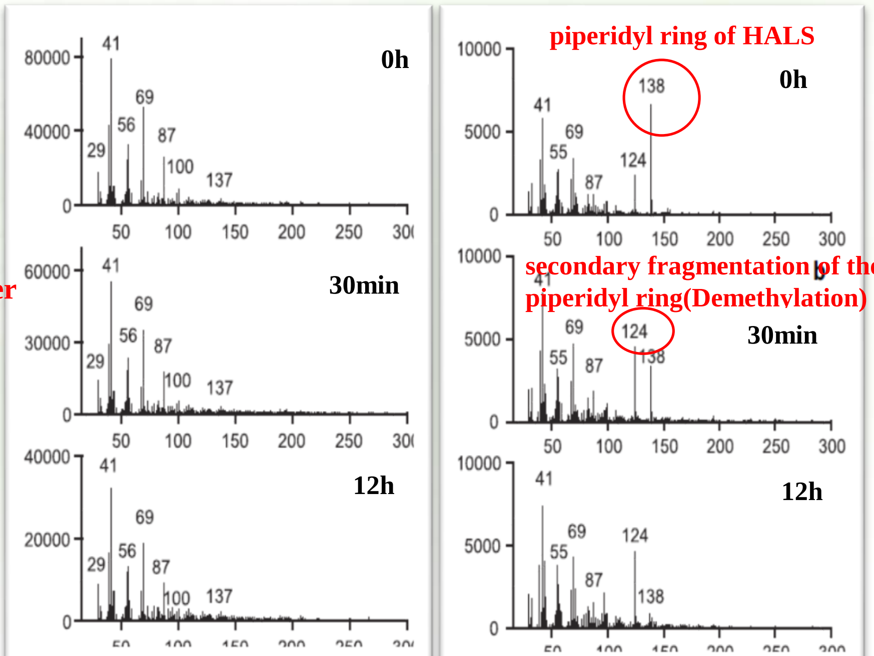


Paint sample

a. Methyl methacrylate (MMA),
b. Butyl acrylate (BA),
c. Butyl methacrylate (BMA)
d. Cyclohexyl methacrylate (CHMA)

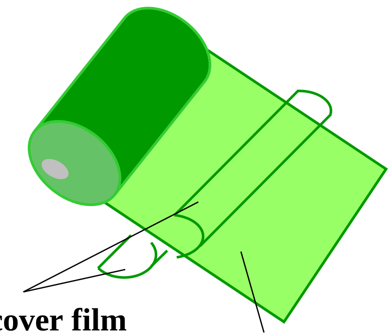




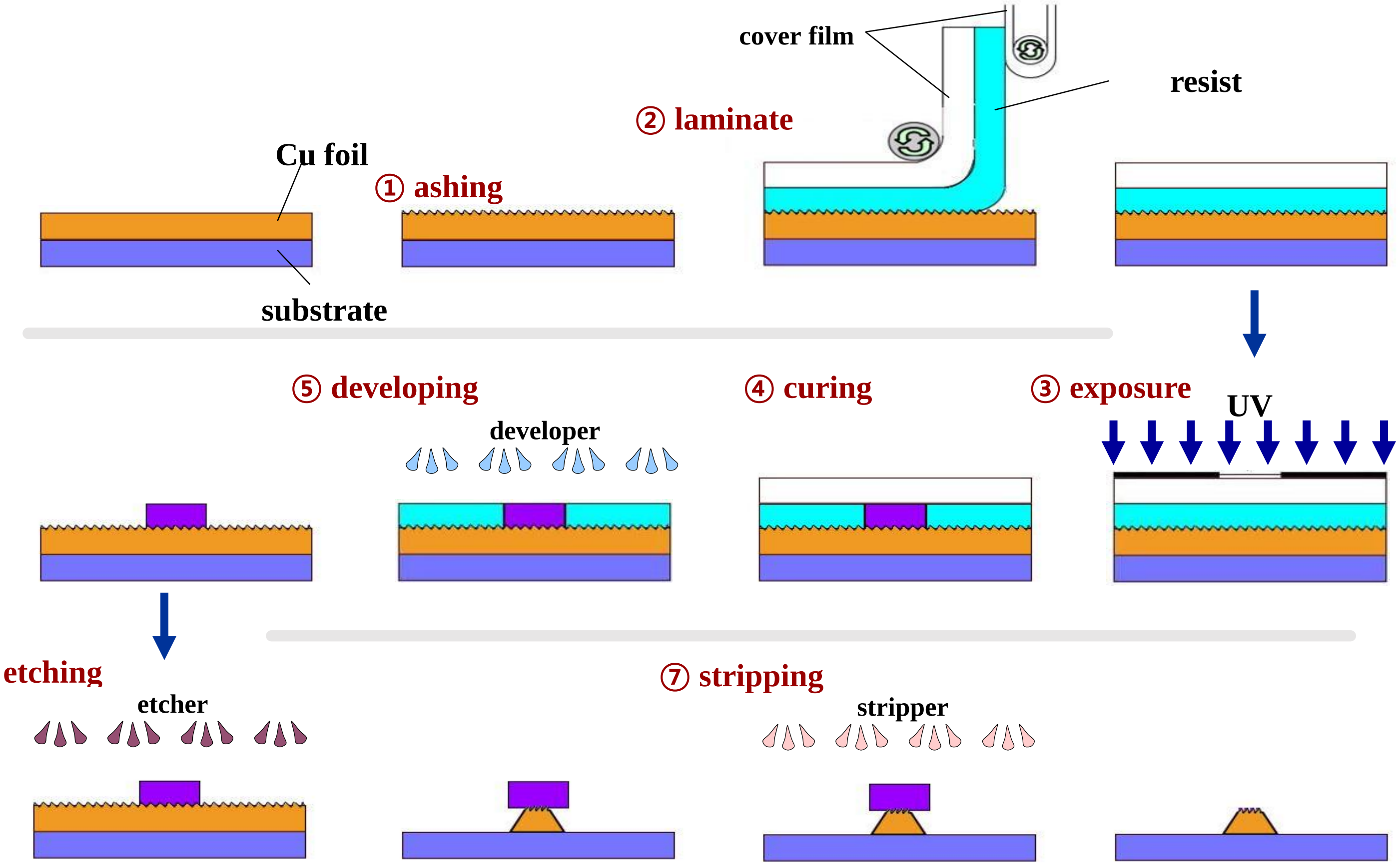


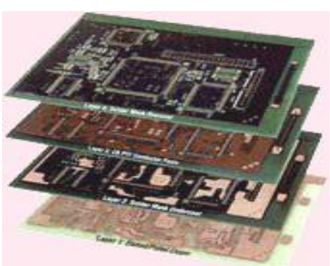
6.2. Example of PR analysis

Photolithography process with dry film resist



Dry film resist



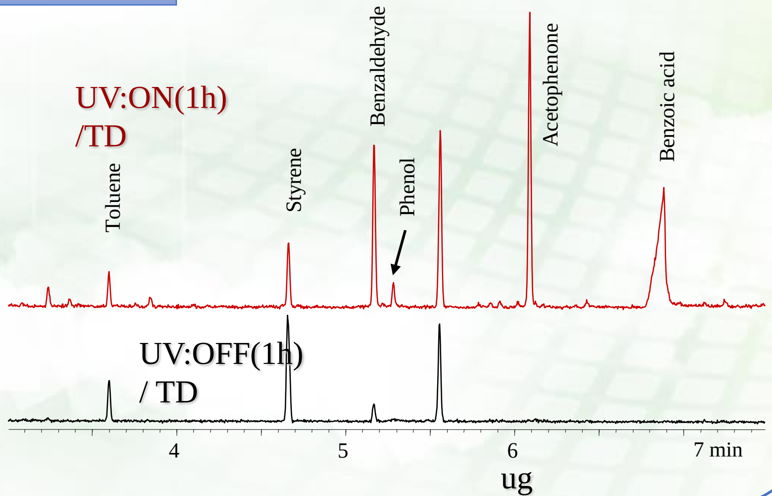


Printed circuit board

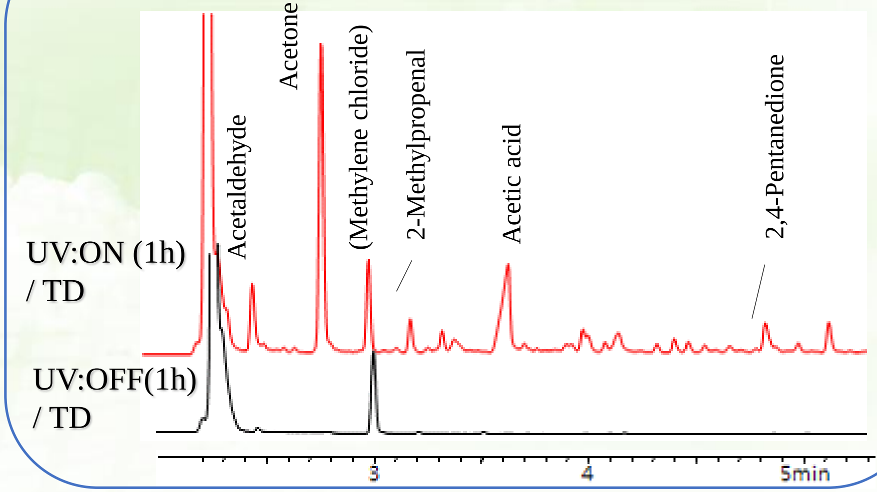
6.3. Example of Out Gas Analysis during UV-Irradiation

UV irradiation at 60˚C for 1-3 hr, Air carrier gas: 10 ml/min, Split ratio: 1/10

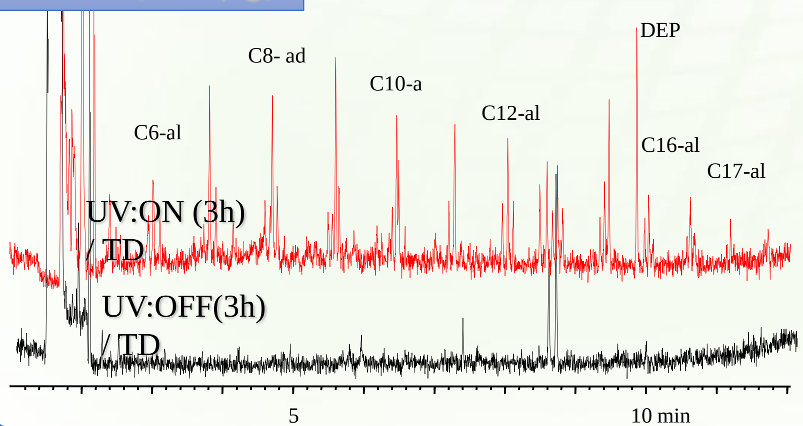
PS (20 μg)



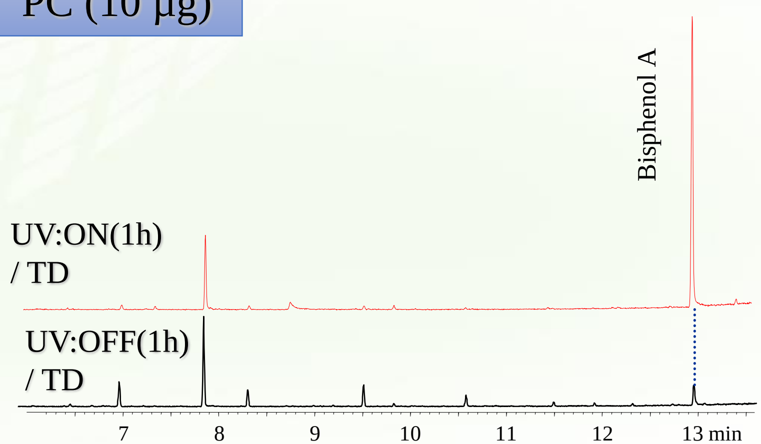
Iso-PP (120 μg)



HDPE (100 μg)



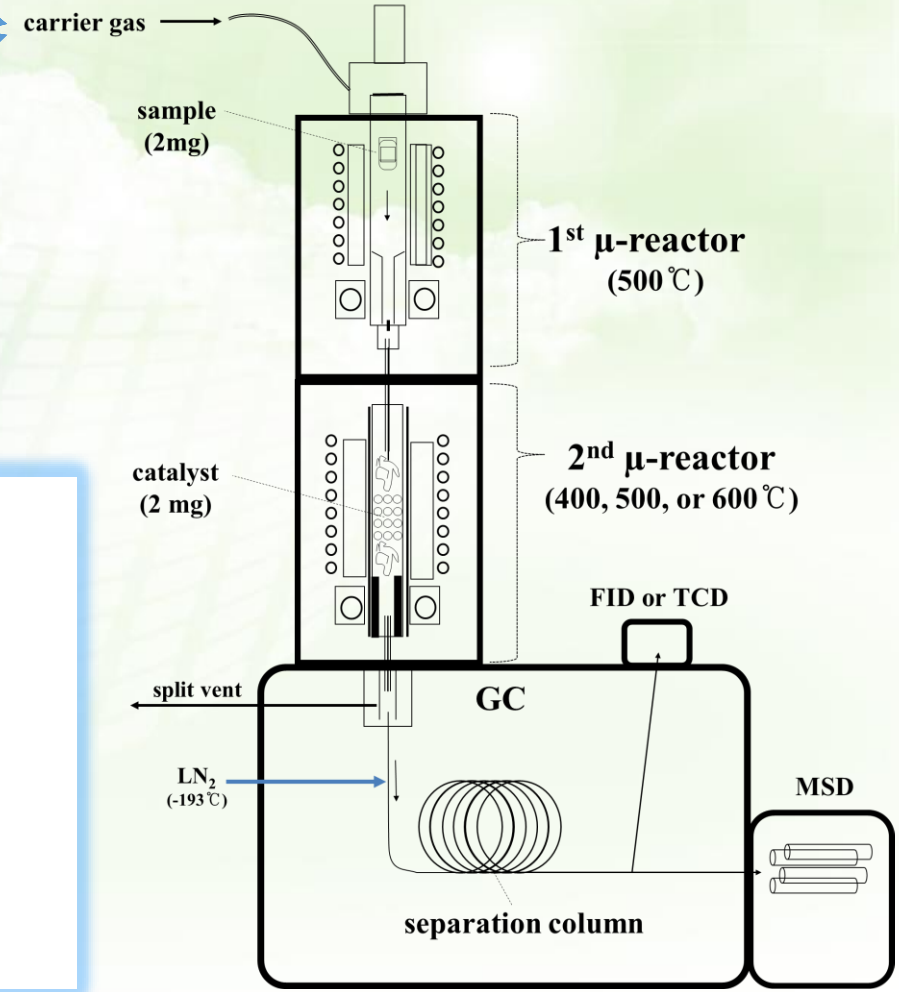
PC (10 μg)



7.2. Tandem micro reactor for the catalytic pyrolysis of polymer

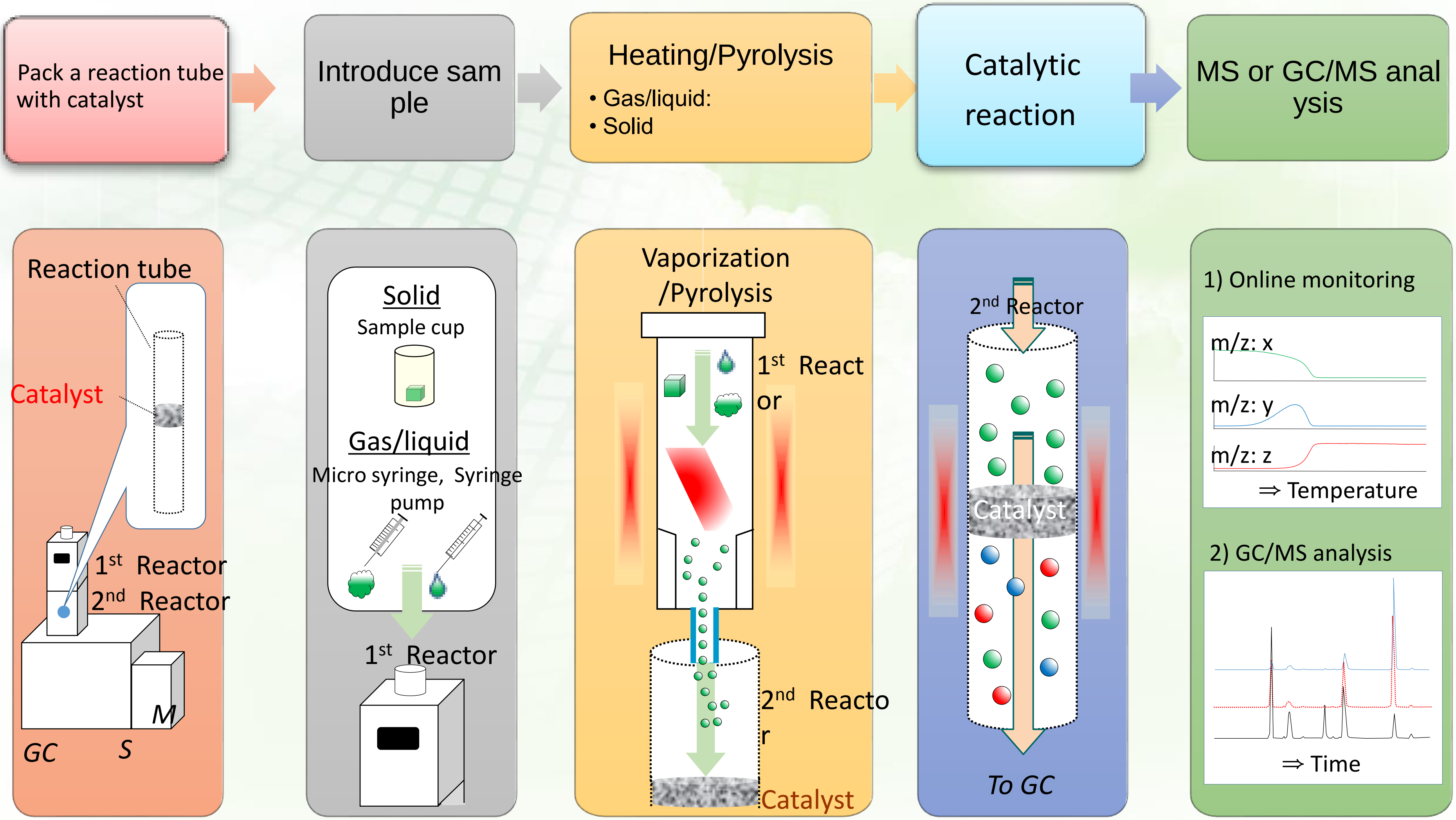
He: Catalytic reaction

Air: Catalyst regeneration



Tandem μ-Reactor
Rx-3050TR

7.2. Overview of rapid catalyst evaluation system with MS detector



7.2. Bio-oil production from waste biomass

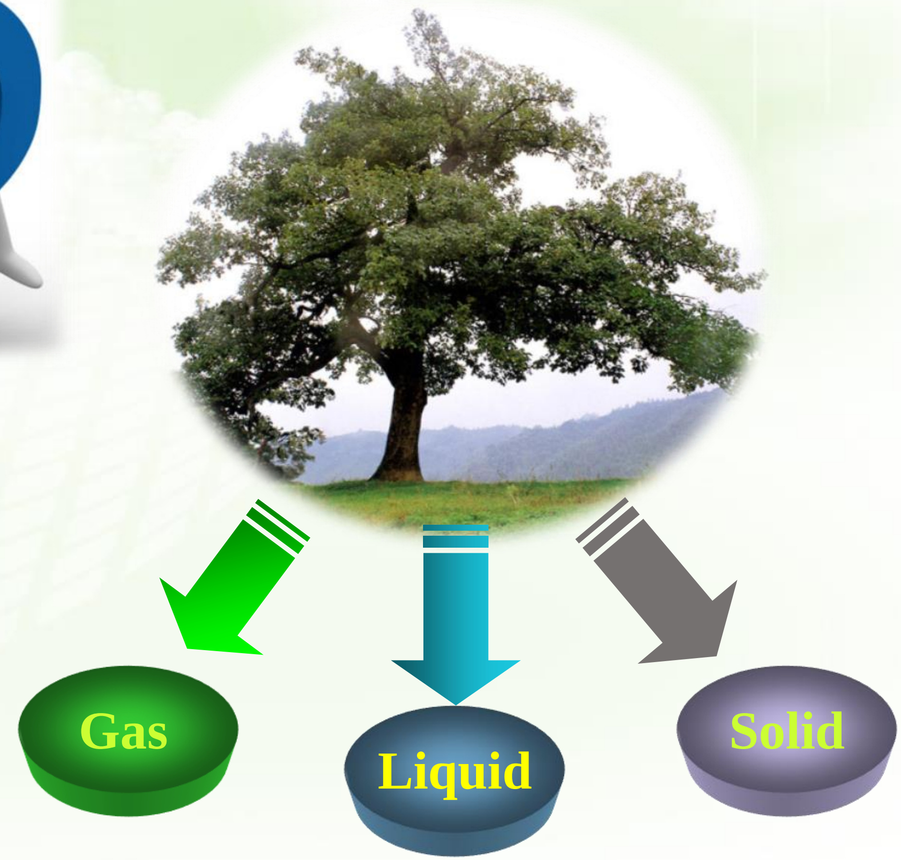
- Bio Energy

Oil shortage

Air contamination

Climate change

Alternative Energy Source

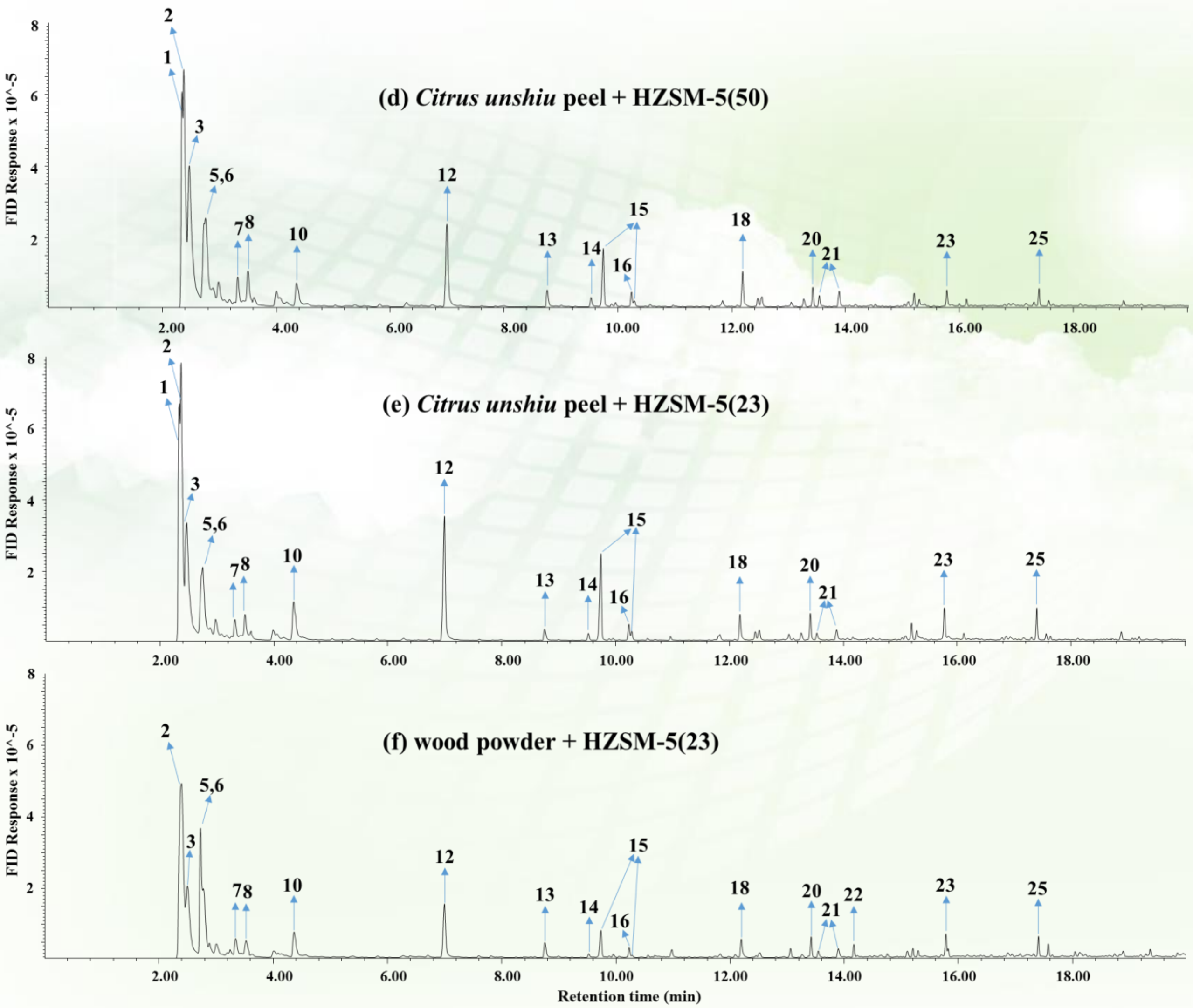


7.2. Bio-oil production from Citrus unshiu peel

Byproducts:
55,000 tons/year in Korea

Citrus unshi peel production:
550,000 tons/year in Korea

7.3. Catalytic upgrading of the pyrolysis products



1: ethene,
2: propene,
3: butene,
4: methanol,
5: furan,
6: acetone,
7: butenone,
8: methyfuran,
9: aceticacid,
10: benzene,
11: hydroxypropanone,
12: toluene,
13: furfural,
14: ethylbenzene,
15: xylene,
16: styrene,
17: methylfurfural,
18: phenol,
19: trimethylbenzene,
20: indene,
21: cresols,
22: guaiacol,
23: naphthalene,
24: pentamethylbenzene,
25&26: methylnaphthalenes

Tandem μ-reactor-GC/FID chromatograms of products produced by catalytic upgrading of pyrolyzates of *Citrus unshiu* peel and wood powder (Pyrolysis at 500°C of 1st μ-reactor, Catalytic upgrading of pyrolyzates at 600°C of 2nd μ-reactor

Changes in appearance of catalyst after experiments

Catalyst in a reaction tube packed with MgO / SiO_2

Fresh

After 2 hours of use
(5% Ethanol in He, 100 ml/min)

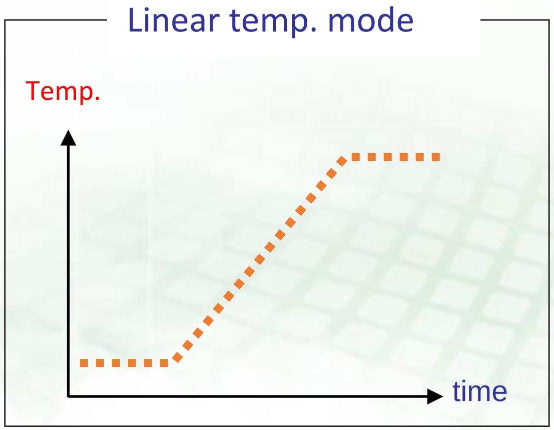
1 mm

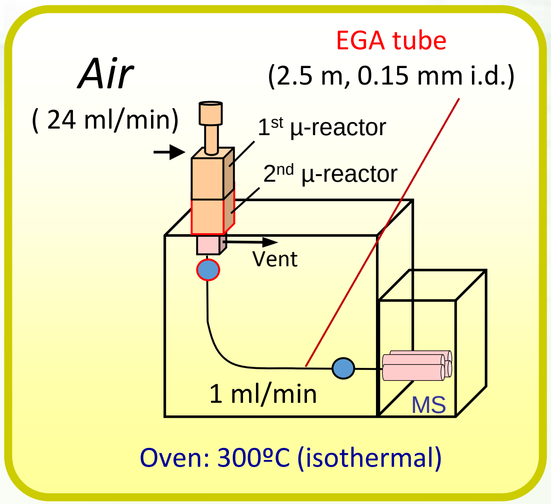
After 6 hours of use
(5% Ethanol in He, 100 ml/min)

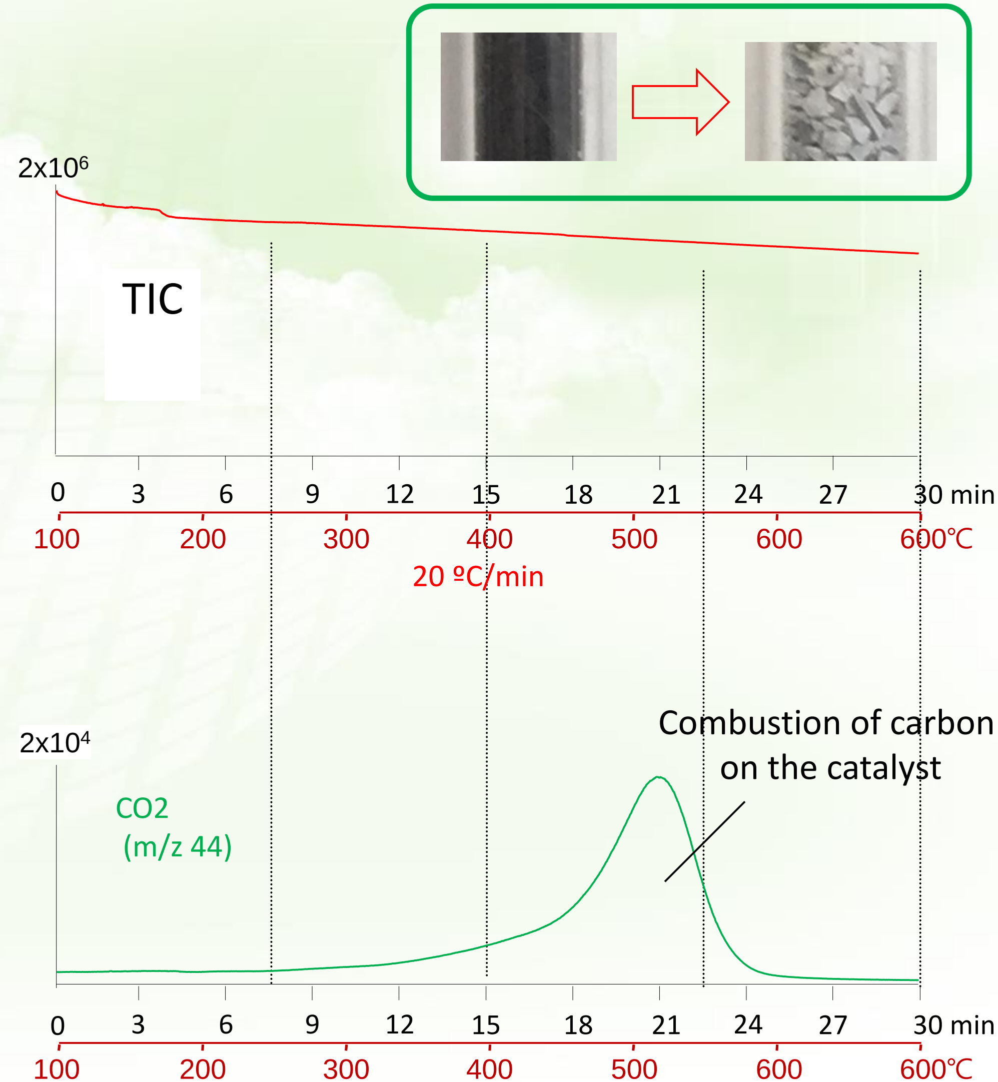
Catalyst : MgO / SiO_2 (Mg / Si = 3 / 4, 35 - 45 mesh)

Study of catalyst decoking process

Catalyst : MgO / SiO_2 (Mg / Si = 3 / 4, 35 - 45 mesh)







1st µ-reactor: 100ºC

2nd µ-reactor: 100-600ºC

(20 ºC/min, 10 min hold)

Thank you for your attention