

## Greater Region Plastic Conference

# Chemical recycling of polymers through catalytic pyrolysis

Sophie DUQUESNE<sup>1\*</sup>, Sophie KLAIMY<sup>1,2</sup>, Carmen Ciotonea<sup>1,23</sup>,  
Jean-François LAMONIER<sup>23</sup>, Mathilde CASETTA<sup>1</sup>, Sophie  
HEYMANS<sup>3</sup>

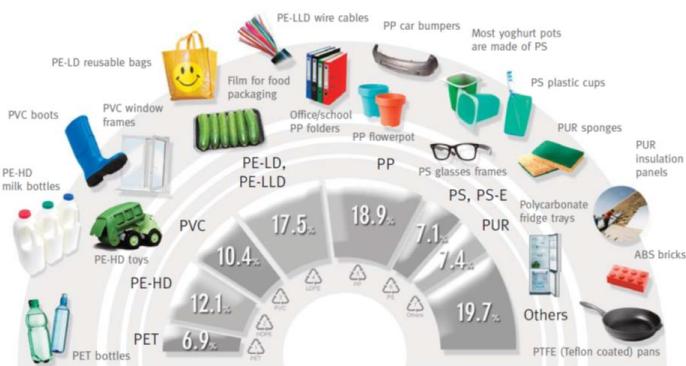


Ce projet est cofinancé par  
l'Union européenne avec  
le Fonds européen de  
développement régional

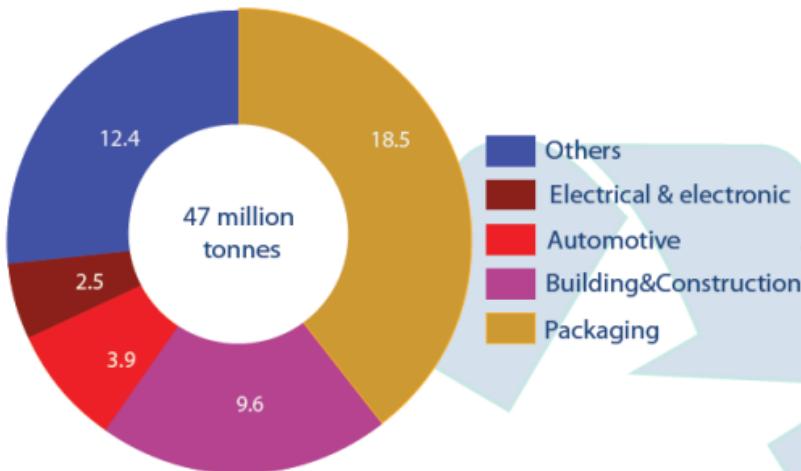


# Plastic wastes

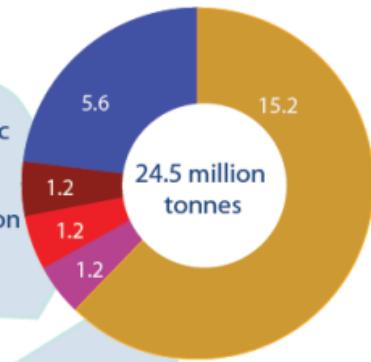
**Plastics production, plastic waste generation by industry and plastic waste treatment by method in the EU, 2011**



Plastics production



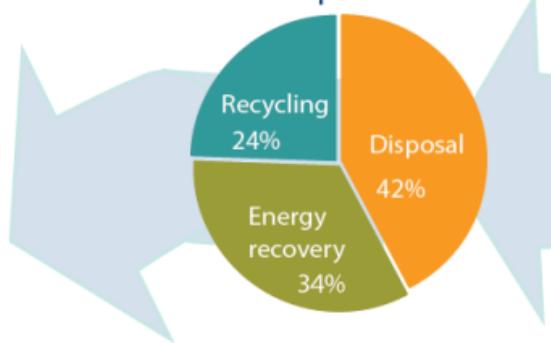
Plastic waste



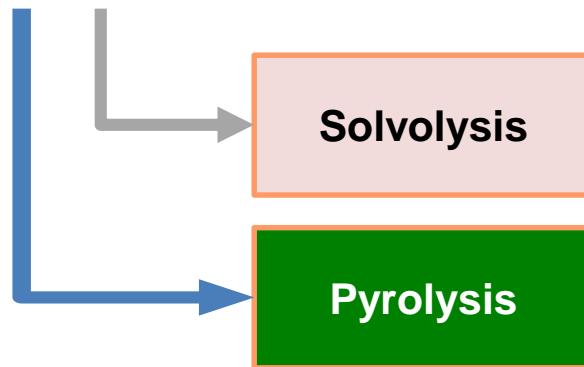
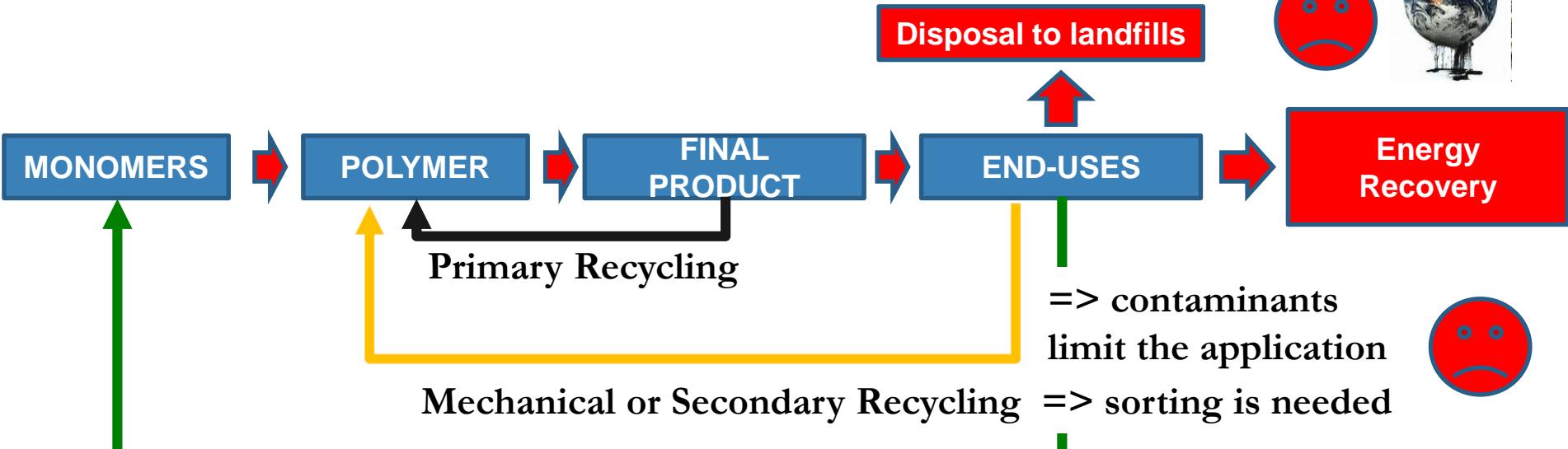
Waste hierarchy



Treatment of plastic waste



## Recycling methods

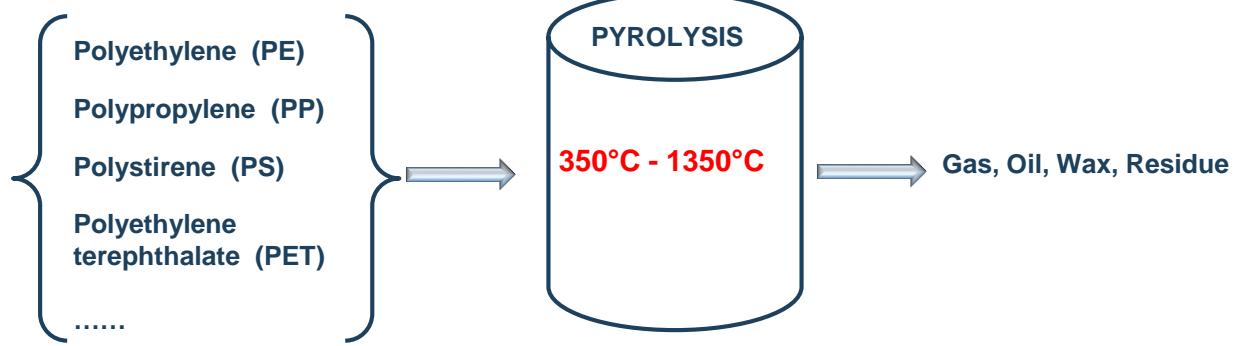


Environmental issues



## What is pyrolysis?

**Environment-friendly process** allowing the valorization of plastic waste by thermal degradation of polymers into smaller valuable molecules



**Thermal degradation mechanism: very complex**

reaction of  $\beta$ -scissiors, isomerization, hydrogen transfer, oligomerization, Diels-Alder addition

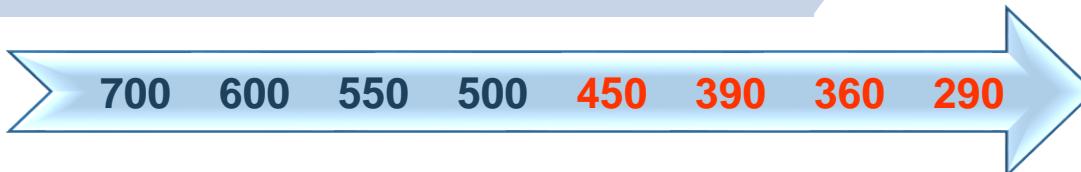


### Drawbacks:

- High temperature of process → high energetically cost
- Low quality of products → making this process unfeasible
- Very wide range of products → complicated processes for separation

## Why catalytic pyrolysis?

**Pyrolysis**

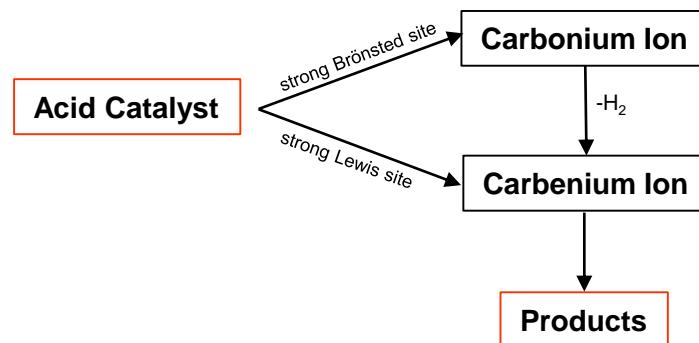


**Catalytic Pyrolysis**

**Acid Catalyst** offer the possibility to orientate the **degradation process** !

**Catalysis Pyrolysis**

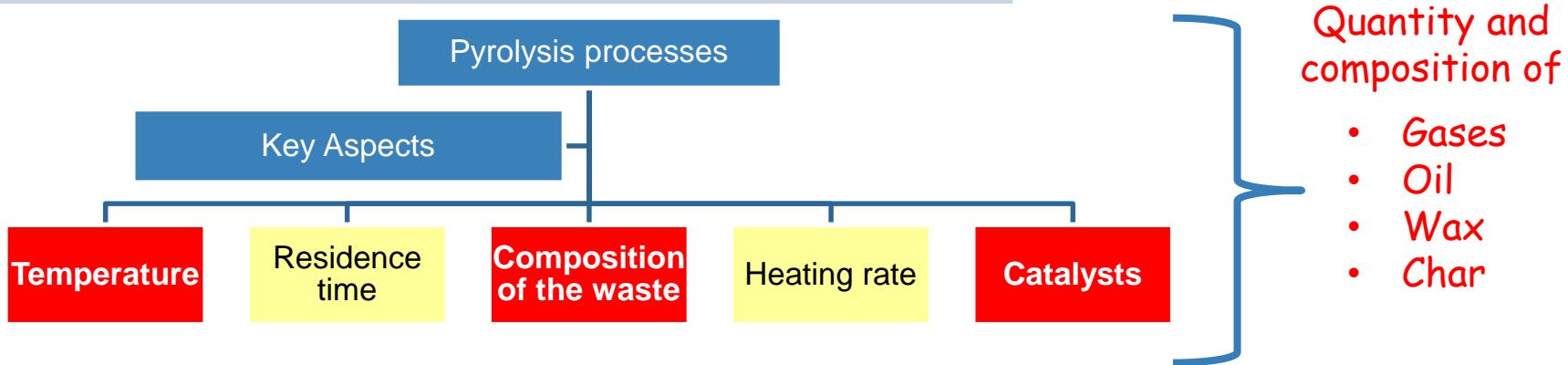
- Less demand in energy
- Less impurities / selectivity
- Decreasing the char residue
- Catalyst : cost and recycling?
- Knowledge on the mechanism of action
- Economic / environmental impact of the processes



**Carbenium Ions promote:**

- charge isomerization
- chain isomerization
- hydride transfer
- alkyl transfer
- formation and breaking of C-C bond

## Content



Data from



	PP	HDPE	LDPE	PS/PET
%	36	9	8	47

	PP	HDPE	LDPE	PS	PET
%	32	29	13	11	15



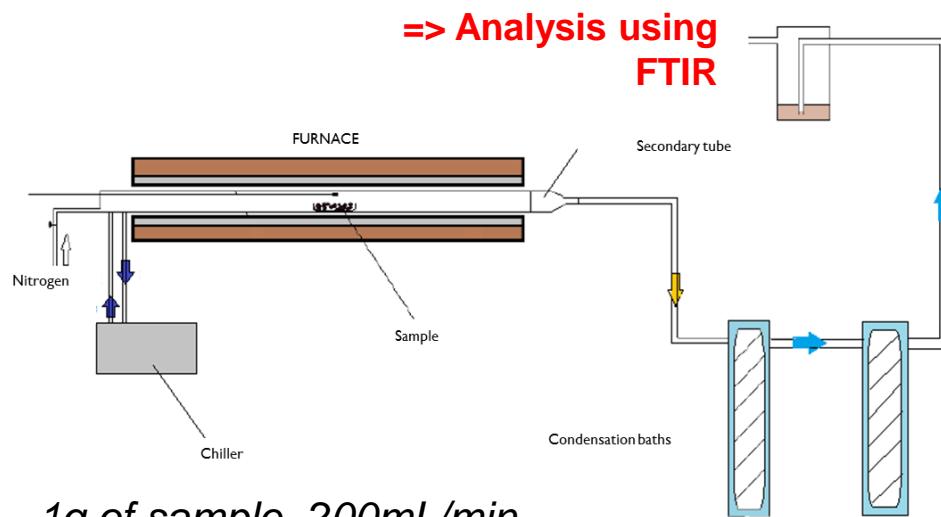
Data from



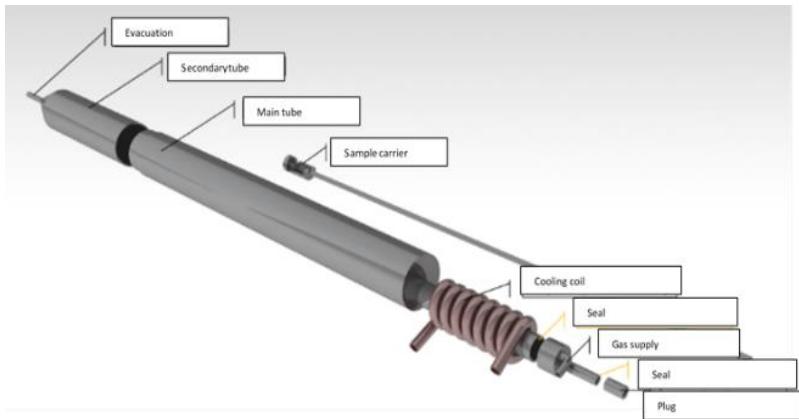
	PP	HDPE	LDPE	PS	PET
%	27	30	17	15	12

Model mixture : **30% PP, 30% HDPE, 15% LDPE, 10% PS, 15% PET**

## Pyrolysis Unit



1g of sample, 200mL/min



**=> Analysis using GC/MS and GS/TCD**

### GC-MS program

Carrier gas: He

Carrier gas flow: 1ml/min

Initial temperature/ initial time: 40°C/15min

Heating rate: 0.5°C/min

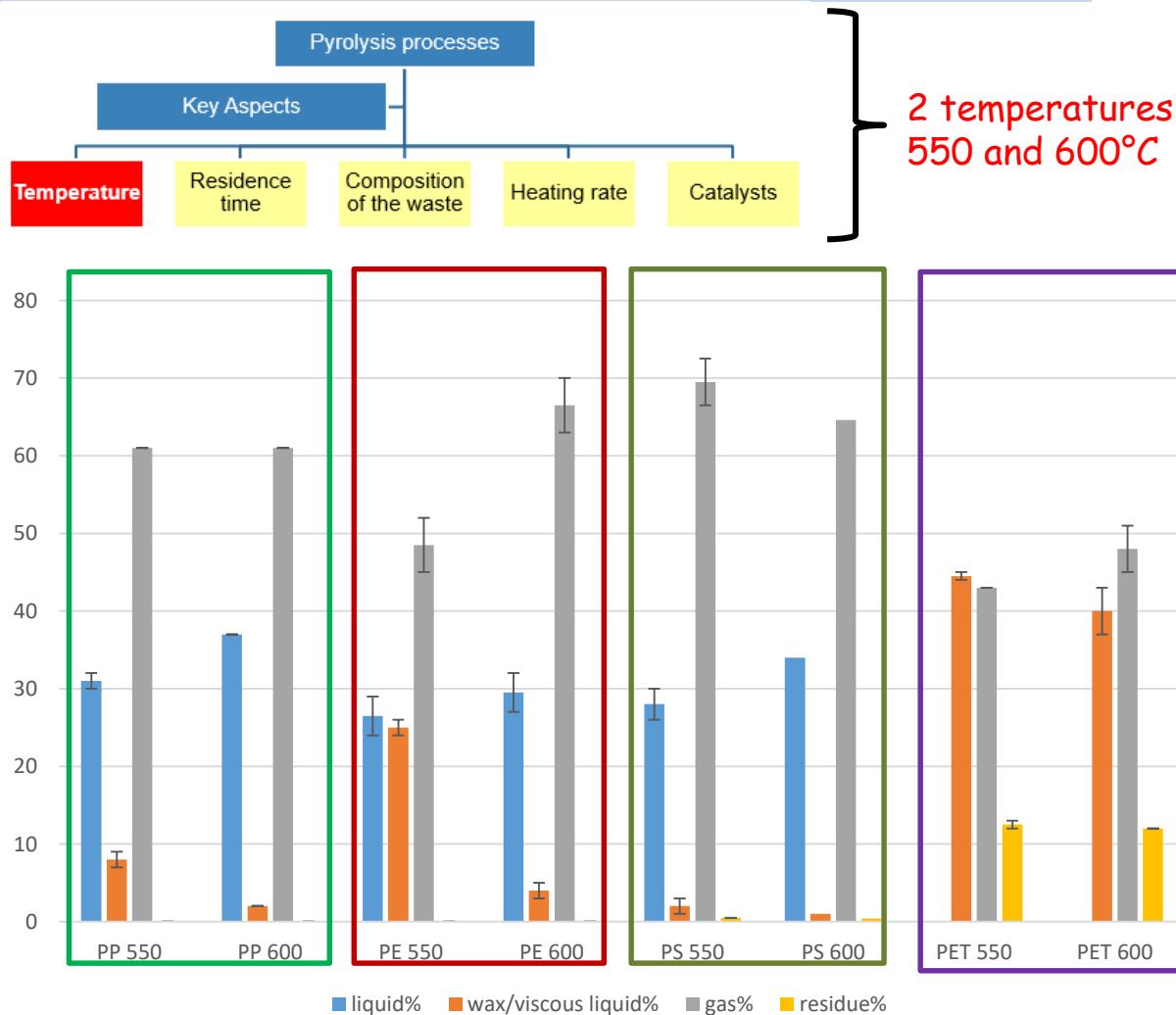
Final temperature/ final time: 160°C/ 15min

Injection temperature: 300°C

Injection volume: split (10:1) split flow: 10ml/min

Transfer line: 300°C

# Thermal Pyrolysis of Virgin Materials



Decreasing of the amount of viscous liquid from 8 to 2% → stronger cracking of C-C bonds

Decreasing of the amount of wax from 25 to 4% → stronger cracking of C-C bonds

PP ≠ PE → easier degradation of PP

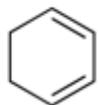
Increasing of the amount of liquid → simple structure of PS

No formation of liquid phase

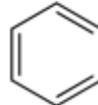
## Composition of condensables in case of PE

**550°C**

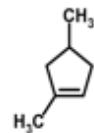
**1,3 cyclohexadiene 5,4%**



**Benzene 10,1%**



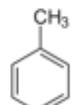
**4,4 dimethylcyclopentene 5,2%**



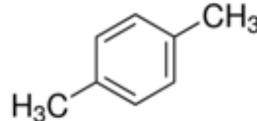
**1,3 cycloheptadiene 6%**



**Toluene 16,9%**

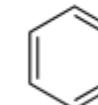


**Xylene 5,1%**

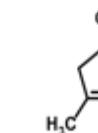


**600°C**

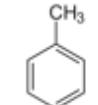
**Benzene 11,2%**



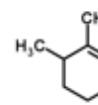
**4,4 dimethylcyclopentene 33%**



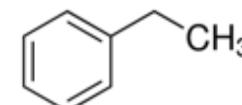
**Toluene 3,9%**



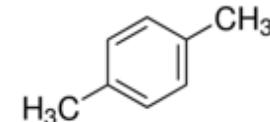
**1,6 dimethyl cyclohexene 4,4%**



**Ethylbenzene 5,7%**



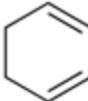
**Xylene 7,5%**

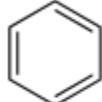


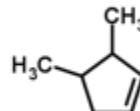
**=> Large amount of aromatic compounds**

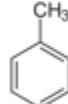
## Composition of condensables in case of PP

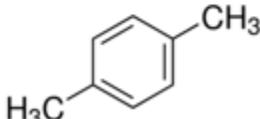
**550°C**

**1,3 cyclohexadiene 4,9%** 

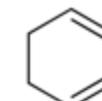
**Benzene 4,9%** 

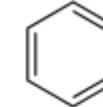
**2,4 dimethyl 1,4 pentadiene 9,7%** 

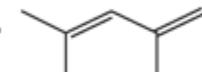
**Toluene 19,3%** 

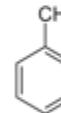
**Xylene 28,4%** 

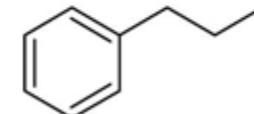
**600°C**

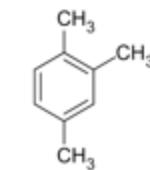
**1,3 cyclohexadiene 7,4%** 

**Benzene 15,3%** 

**4,4 dimethylcyclopentene 5,2%** 

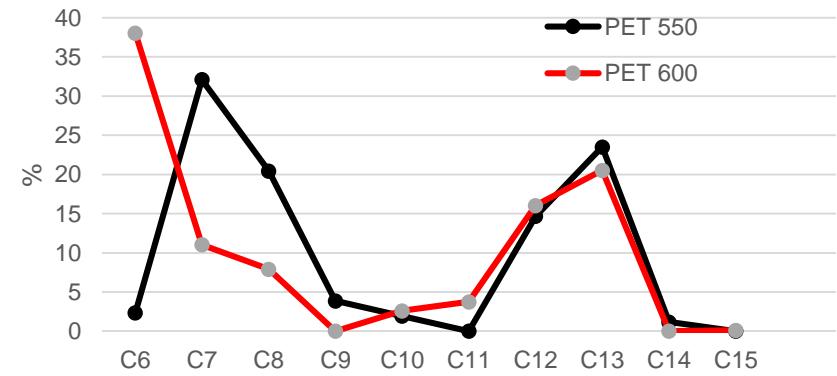
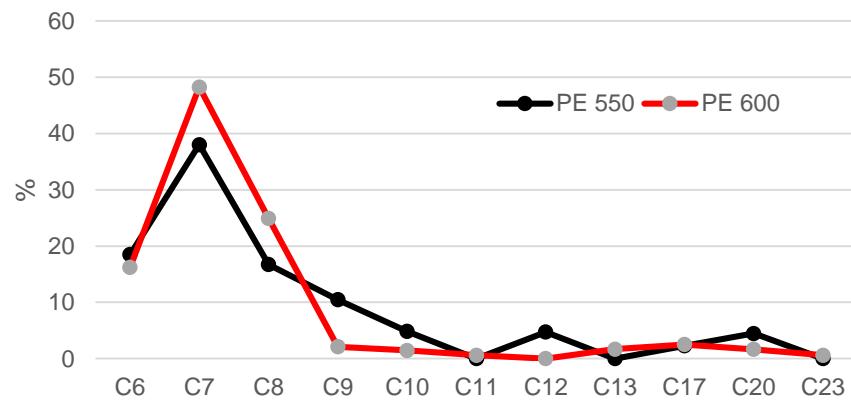
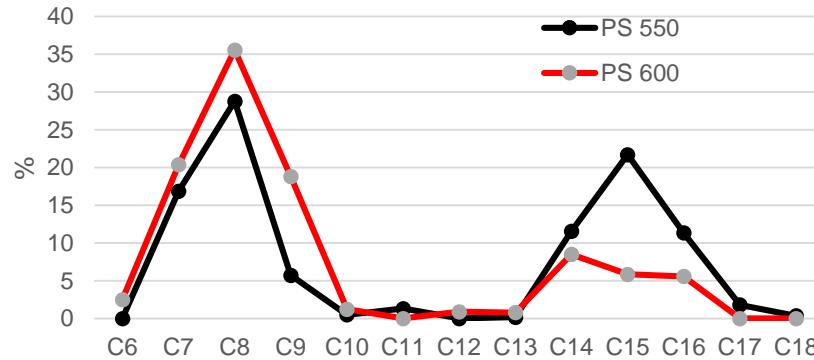
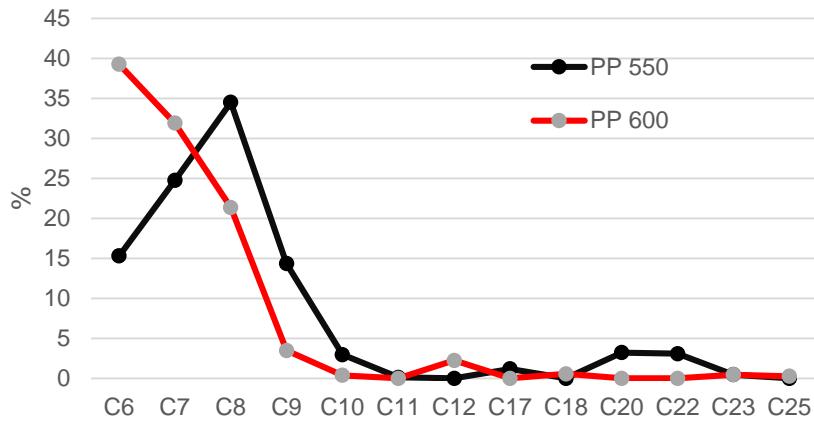
**Toluene 25,8%** 

**Propylbenzene 6,5%** 

**1,2,4 trimethylbenzene 4,7%** 

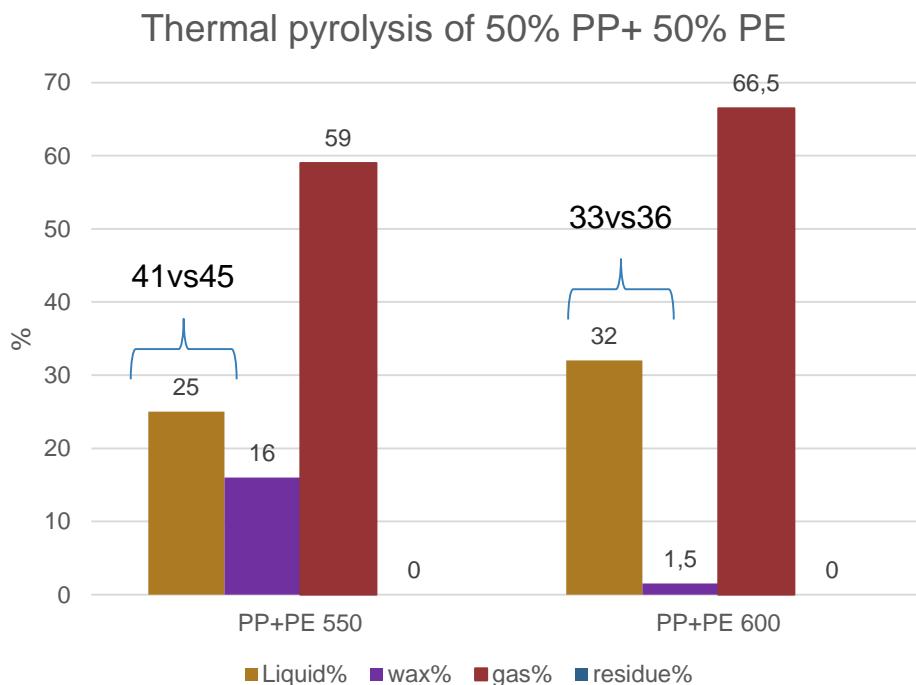
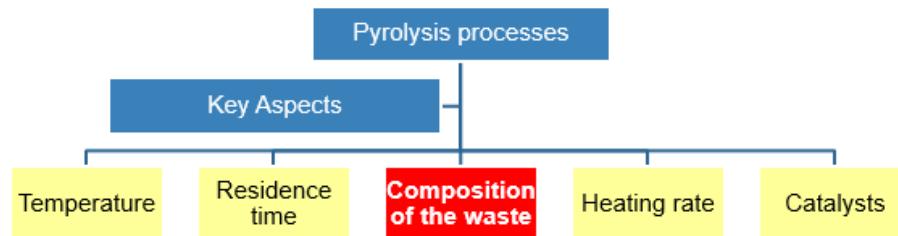
↑ Temperature => ↑ aromatic compounds

## Effect of temperature on oil composition



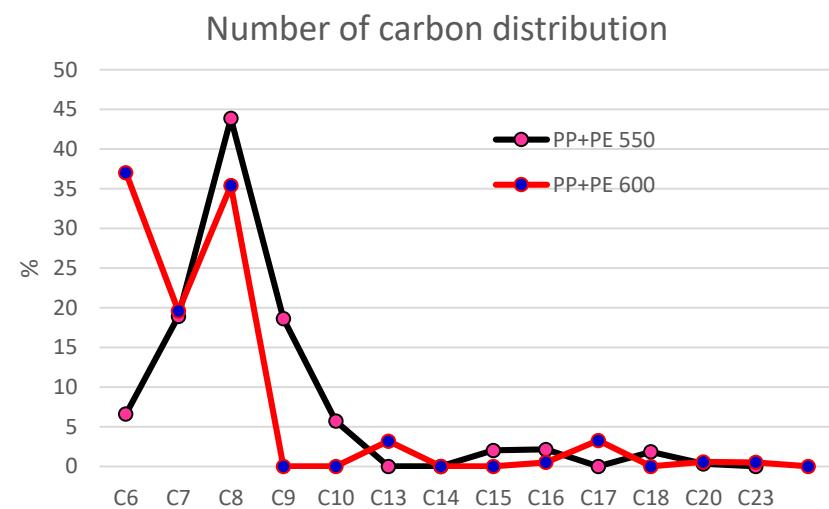
↑ Temperature => ↓ number of C in the condensable products

# Thermal pyrolysis of mixtures

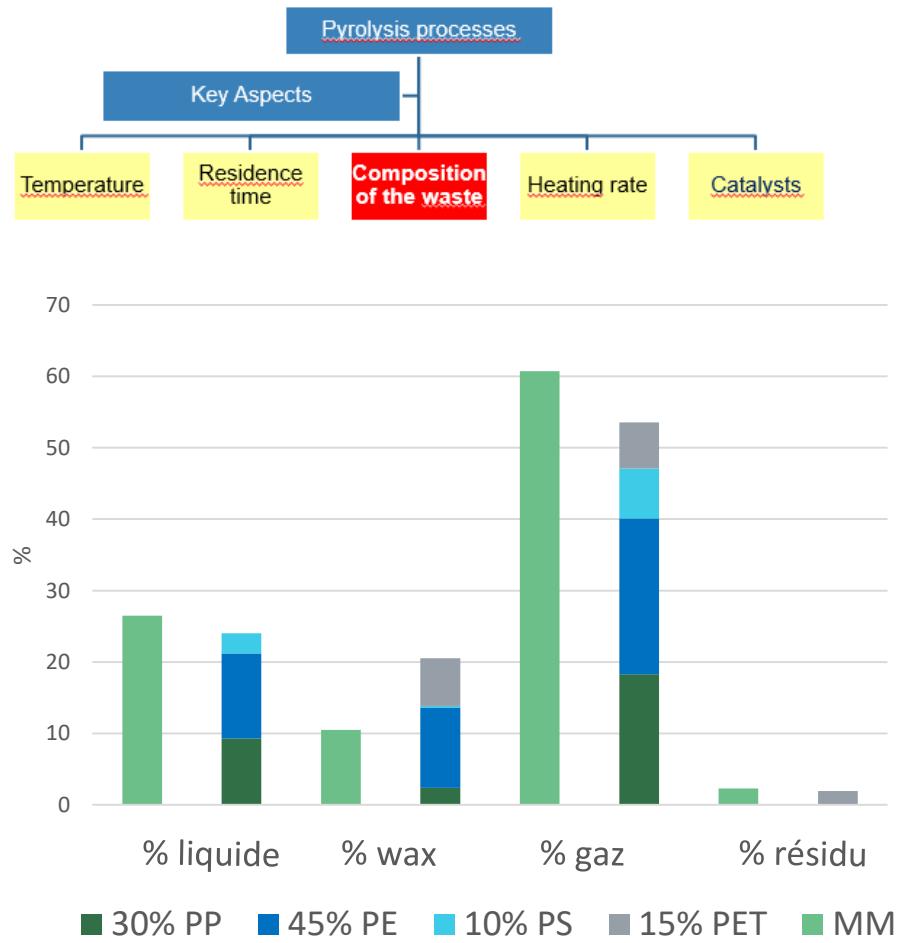


PE/2	550 °C	600 °C
Liquid+wax%	26	17
Gaz%	24	33

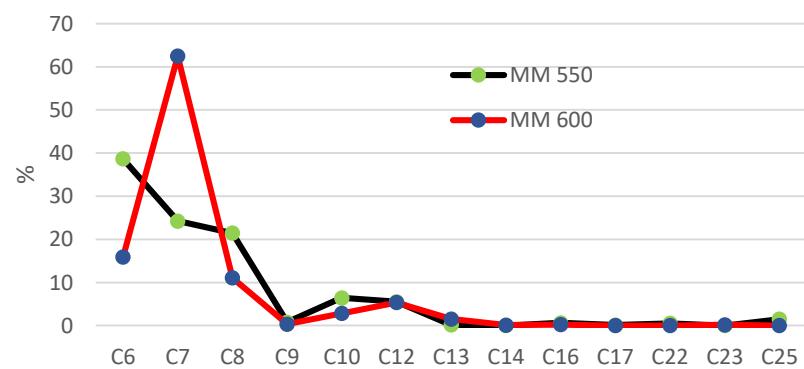
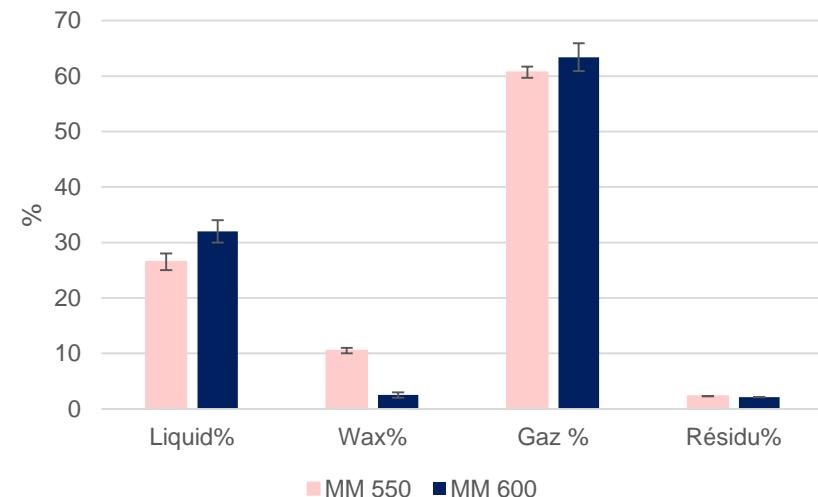
PP/2	550°C	600 °C
Liquid%	19	19
Gaz%	31	31



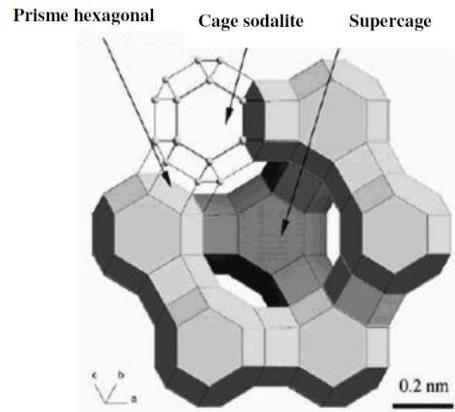
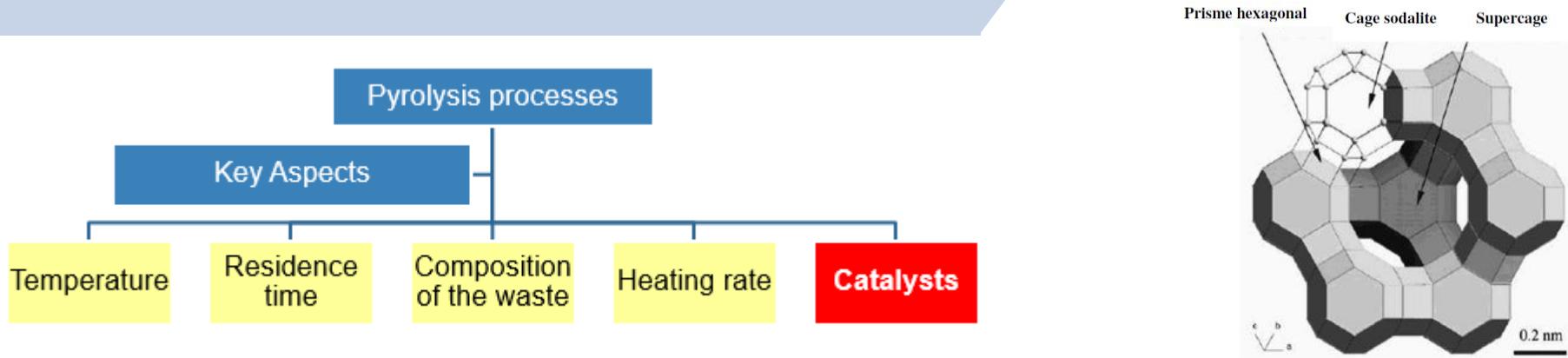
# Thermal pyrolysis of mixtures



Thermal pyrolysis of the model mixture



# Literatur review - Acid catalyst used in catalytic pyrolysis of plastic waste



**Acid catalyst:** zeolites (ZSM-5, HY, Beta-Y, HNZ), mesoporous silica (MCM-41), clays, NiFe CNTs

Sample	Ratio Si/Al	$S_{BET}$ (m <sup>2</sup> /g)	PYROLYSE				Ref.	
			Substrate/ catalyst	Temperature (°C)	Yield wt %			
					Gas	Liquid		
ZSM-5 Penta-H	22	379	PE/ 10 wt.%	450	88,4	10,9	0,7	Park et al.
ZSM-5 Süd Chemie Corporation	35	397	PE/ 30 wt%	450	77,88	22,12	0	Mastral et al.
ZSM-5 BP Chemicals	17	391	PE / 40 wt. %	360	94,21	1,26	4,53	Lin et al.
ZSM-5 GRACE-Davison	-	341	PE / 10 wt. %	550	70,7	18,3	0,5	Marcilla et al.

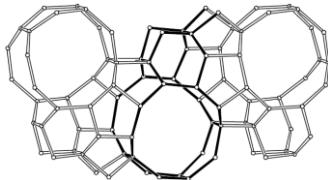
**Catalyst parameters:** Acidity, crystallite size, porosity size

## Zeolites: ZSM-5 ; acidic materials

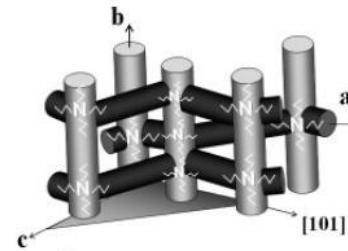
→ Hydrates aluminosilicates with microporous and crystalline structure- type MFI (Mobile Five), formed by uniform tetrahedral units (Primary Building Unit, PBU)

**ZSM-5:**  $|\text{Na}_n (\text{H}_2\text{O})_{16}[\text{Al}_n \text{Si}_{(96-n)}\text{O}_{192}]|$ -MFI, avec  $n < 27$

- orthorhombic symmetry structure, being composed of 96 tetrahedra defining a 3D network, including straight and sinusoidal interconnected channels
- two diameters of pores :  $d_1 = 5.1 \text{ \AA}$ ,  $d_2 = 5.5 \text{ \AA}$



view on a sinusoidal channel of MFI



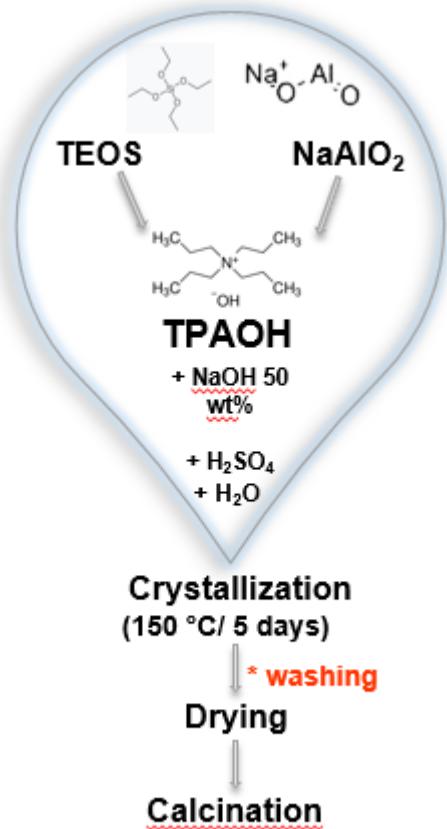
straight and sinusoidal  
interconnected channels of MFI

### ZSM-5 with different parameters:

**Acidity:** - ratio Si/Al 5 -  $\infty$  can be obtained by direct synthesis;  
- post treatments : desilication or dealumination;

**Structural and morphological:** - crystallite size  
- micro or mesoporosity

## Experimental part : h-ZSM-5

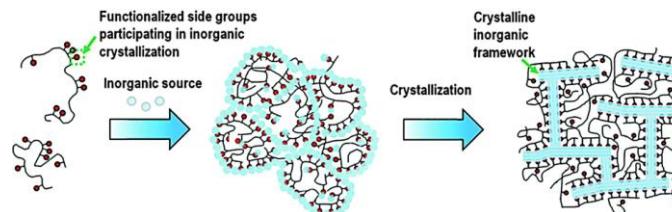


**Molar Composition:**

$$100 SiO_2 : xAl_2O_3 : 30Na_2O : 16H_2SO_4 : 20TPAOH : 4000H_2O$$

$$x = 0.43; 0.77; 1.0; 2.30$$

**Crystallization:**



**Washing: → pH ~ 8**

**Ion exchange:  
→ h-ZSM-5**

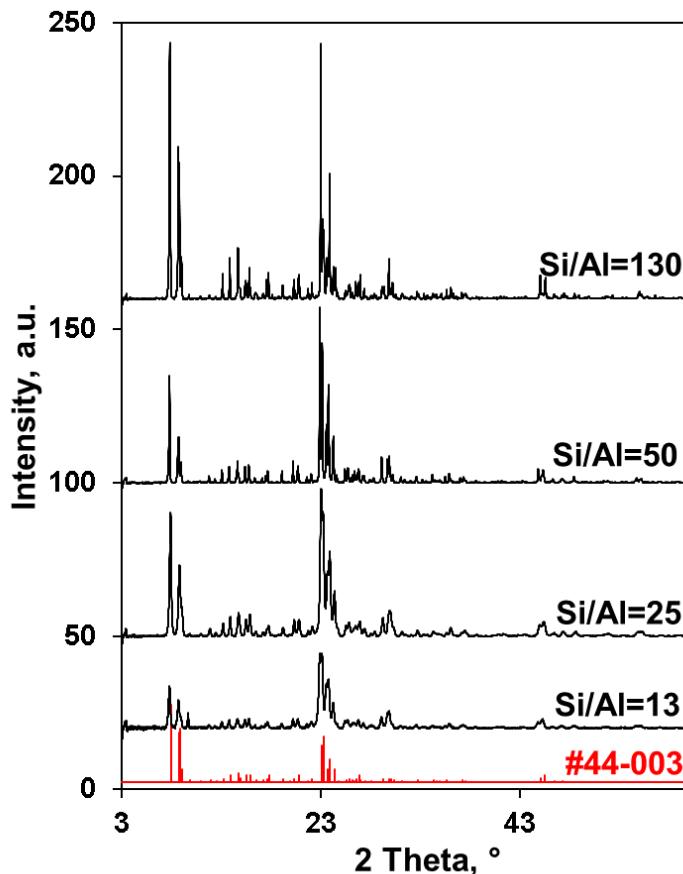
**Filtration - with Buchner /centrifugation**  
**Calcination - 550 °C for 8h**

Calcined Na-ZSM-5 was ion exchanged with 0,5 M  $NH_4NO_3$ , 70 °C /6h ; filtrated, washed, dried (100 °C/24h) and calcined.

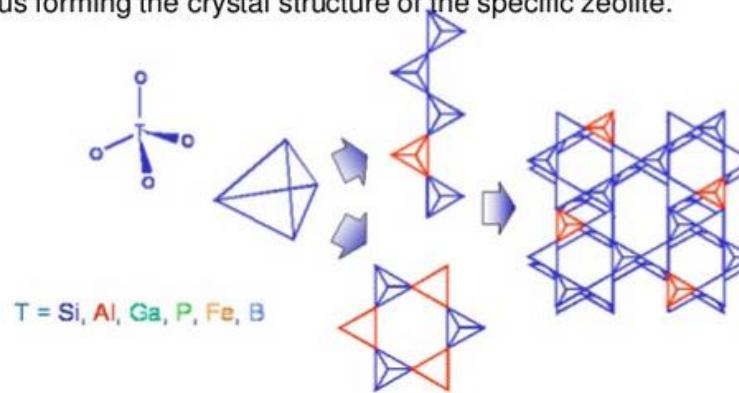
**In this work: h-ZSM-5 was prepared having the ratio Si/Al = 13, 25, 50 and 130**

# Structural and morphologic analysis for h-ZSM-5

## X-ray diffraction



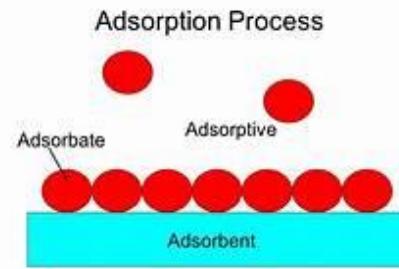
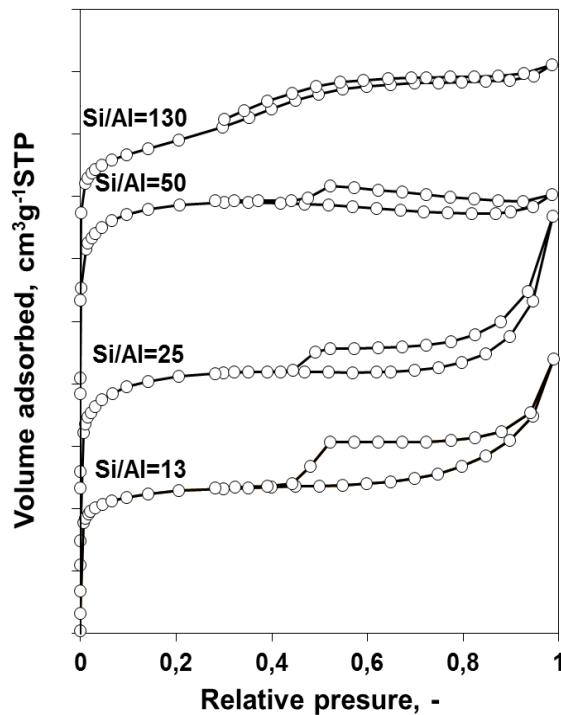
The primary building unit of zeolites are cations coordinated tetrahedrally by oxygen. These tetrahedra are connected via corners, thus forming the crystal structure of the specific zeolite.



- ✓ Typical reflections associated to MFI structure  
→ h-ZSM-5 was successfully prepared
- ✓ No broad peaks at  $2\Theta = 20$  to  $25^\circ$   
→ well crystallized h-ZSM-5

## Structural and morphologic analysis for h-ZSM-5

### *N<sub>2</sub>- Physisorption*



There are three parameters used to measure porosity; specific surface area, specific pore volume or porosity, and pore size and its distribution.

$$\text{Specific Surface Area, m}^2/\text{g} = \frac{\text{Total surface area, m}^2}{\text{Mass of the solid, g}}$$

$$\text{Porosity, \%} = \frac{\text{Volume of pores}}{\text{Volume of solid (including pores)}} \times 100$$

$$\text{Specific Pore volume, cm}^3/\text{g} = \frac{\text{Total pore volume, cm}^3}{\text{Mass of the solid, g}}$$

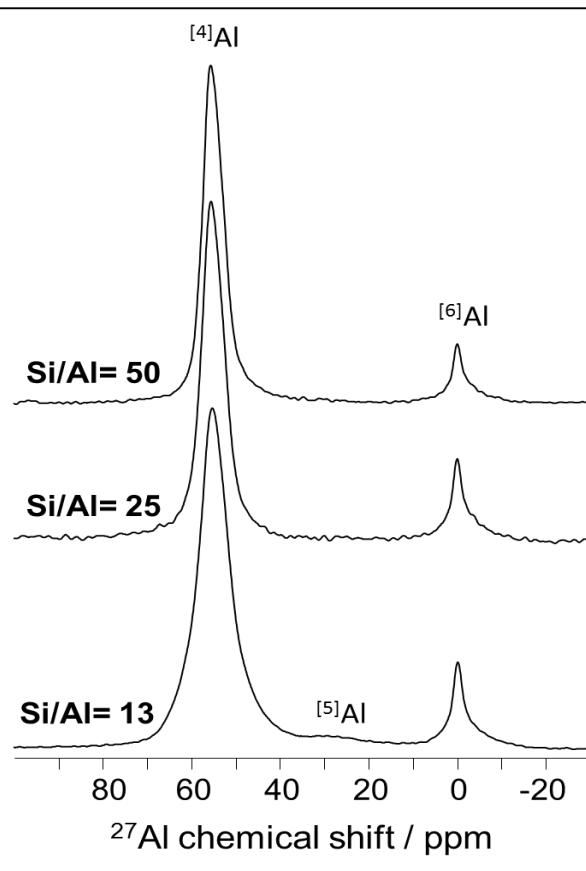
Source : Horiba

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>micro</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm <sup>3</sup> /g)
Si/Al= 13	185	165	0.11	0.0883
Si/Al= 25	284	249	0.17	0.1335
Si/Al= 50	292	260	0.13	0.1228
Si/Al= 130	270	218	0.15	0.1152

- ✓ V<sub>P</sub> of 0,13 and 0,21 cm<sup>3</sup>/g and S<sub>BET</sub> of 185 and 294 cm<sup>2</sup>/g confirms a well crystalized structure of the h-ZSM-5

## Structural and morphologic analysis for h-ZSM-5

**RMN  $^{27}\text{Al}$**



- ✓ The presence of tetrahedral and octahedral Al is revealed
- ✓ ~ 90 % of  $[4]\text{Al}$  is into zeolite framework for all the samples

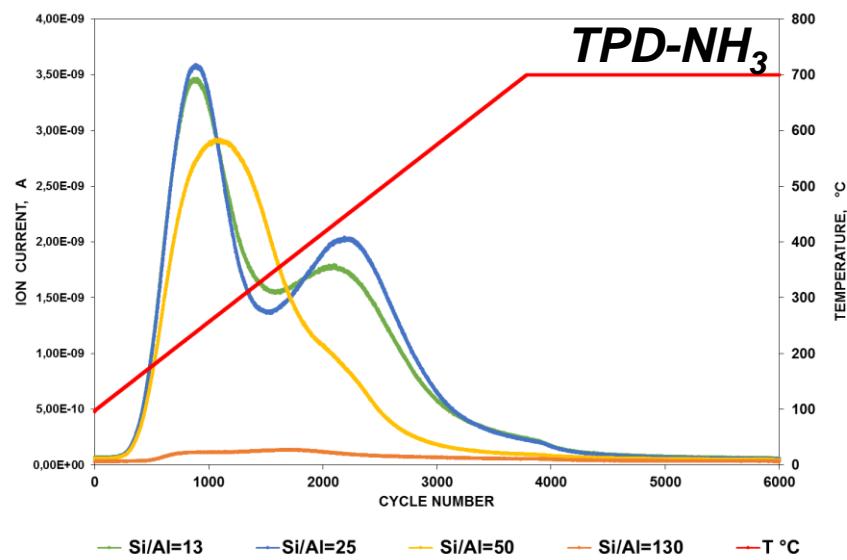
Sample	% $[4]\text{Al}_{\text{fw}}$	% $[5]\text{Al}$	% $[6]\text{Al}_{\text{bulk}}$
Si/Al = 50	92 +/- 5	0	8 +/- 3
Si/Al = 25	89 +/- 5	0	11 +/- 3
Si/Al = 13	91 +/- 5	1 +/- 3	8 +/- 3

The  $^{27}\text{Al}$  MAS-NMR experiments were performed at 208.5 MHz on a AVANCE III 18.8T spectrometer equipped with a 3.2 mm probehead operating at spinning frequencies of 20-22 kHz. The quantitative spectra were acquired with a 1  $\mu\text{s}$  pulse length, 512 transients and a recycle delay of 0.5 s. The  $[x]\text{Al}$  quantification was directly obtained by signal integration.

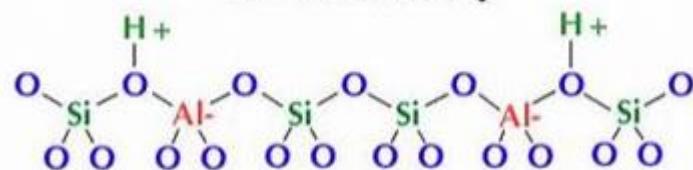
## Acidity of h-ZSM-5

**FTIR-Py and TPD-NH<sub>3</sub>**

**FTIR-Py –analyze the type of acidity**  
**TPD-NH<sub>3</sub> –analyze the force of acidity**



*Brønsted Acidity*

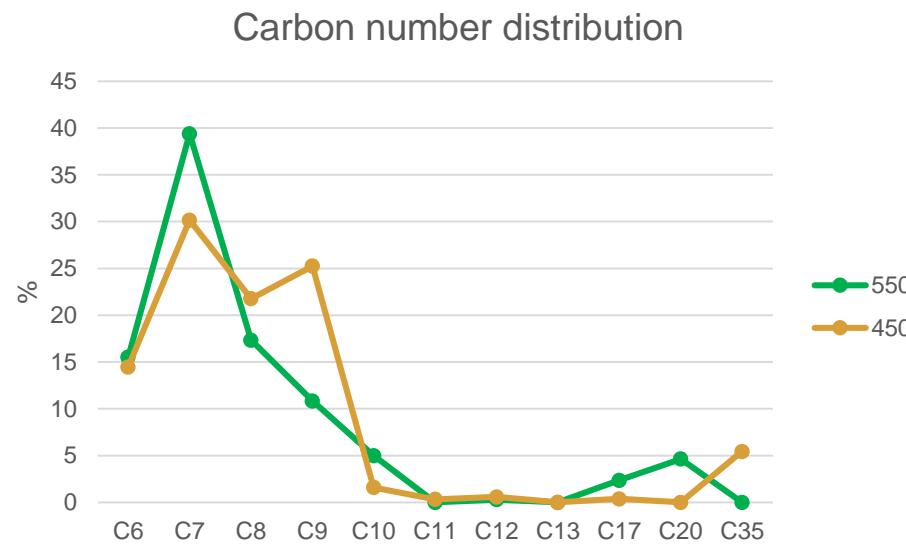
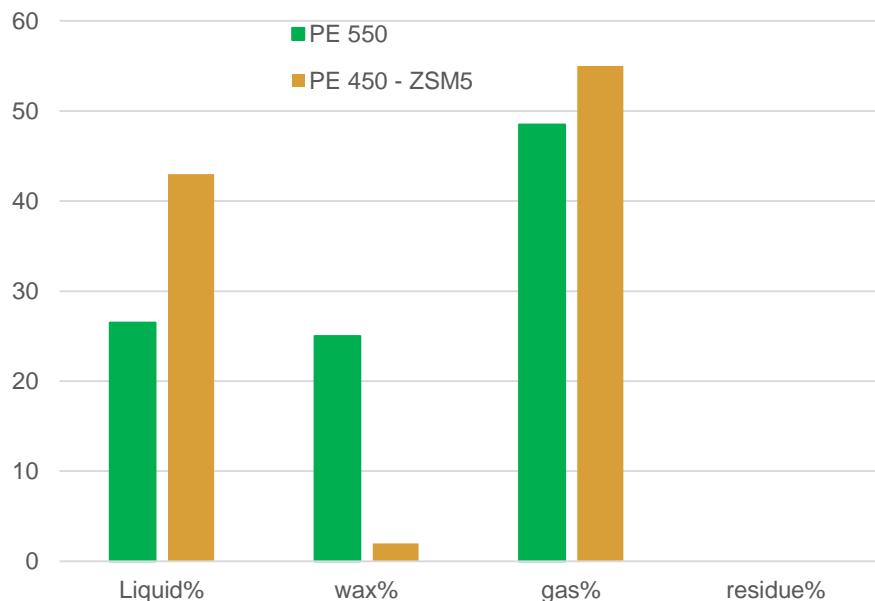


- ✓ Strong acid sites are obtained for Si/Al ratio of 13 and 25

Brønsted acidity: 50 < 25 < 13

Sample	Acidity (probe: NH <sub>3</sub> ) (mmol/g)	Acidity (probe: Pyridine) (mmol/g)
		ratio Brønsted / Lewis
Si/Al= 13	1.83	1.21
Si/Al= 25	2.16	6.90
Si/Al= 50	1.80	4.53
Si/Al= 130	0.10	-

## Catalytic pyrolysis of polyethylene

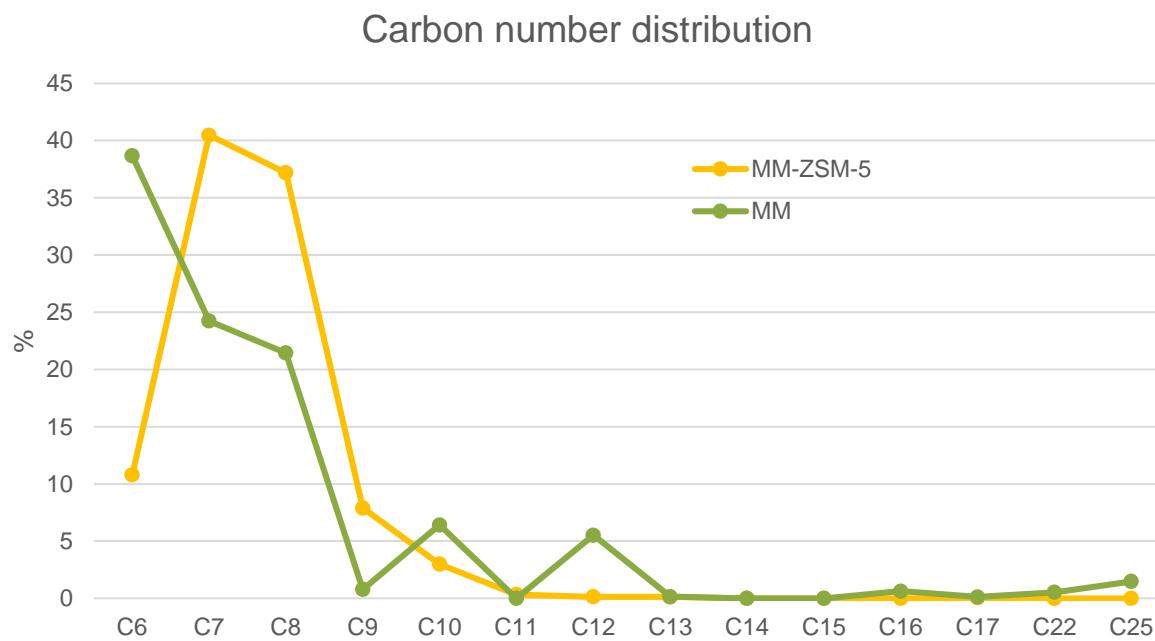


### Catalytic Pyrolysis:

- ✓ High yield of liquid phase
- ✓ High decreasing of wax formation
- ✓ Strong Brönsted acidity of ZSM-5 zeolite has a great influence in aromatization reactions (C6-C9)

## Catalytic pyrolysis of MM at 550°C

	Thermal	ZSM-5
Liquid%	26,5	34
Wax%	10,5	6,9
Gas%	60,7	58,8
Résidue%	2,3	0,3



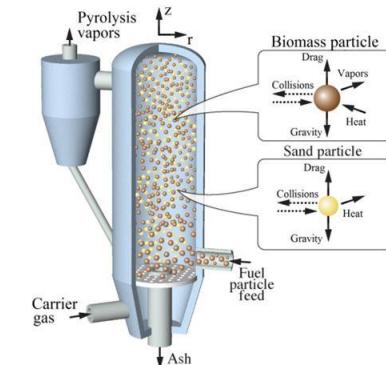
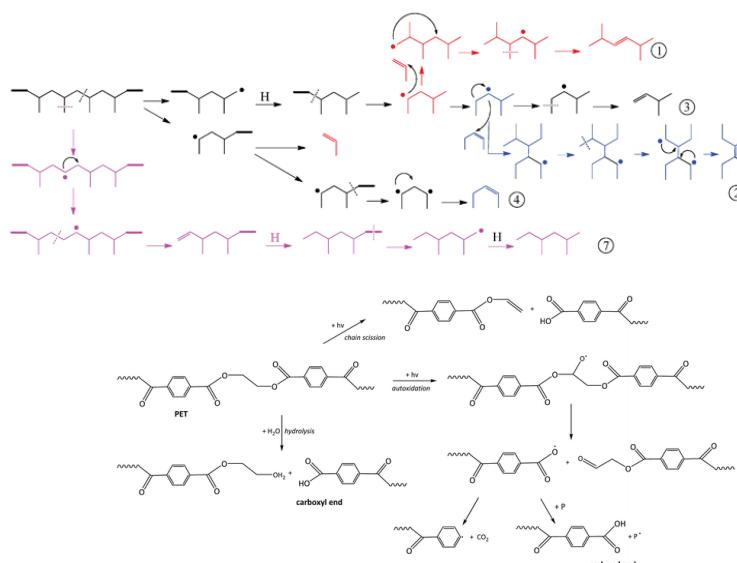
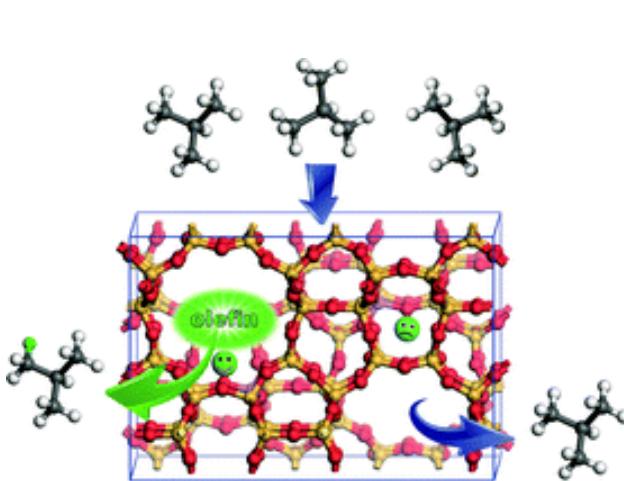
**% C6-C8:**

84% MM THERMAL →  
53% benzene + toluene  
+ styrene

87% zsm-5 → 71%  
benzene + toluene +  
styrene

## Conclusions

- ❖ Pyrolysis is a promising way to recycle plastic wastes
- ❖ All h-ZSM-5 samples are showing MFI structure well crystallized
- ❖ Catalytic Pyrolysis of Polyethylene is presenting high yields to liquid phase (40 wt.%) compared to Thermal Pyrolysis (26 wt.%) and a high decreasing in wax formation
- ❖ Strong Brönsted acidity of ZSM-5 zeolite has a great influence in aromatization reactions, the liquid phase is containing a majority of aromatic molecules



# Thank you for your attention!

Acknowledgment to the Région Hauts de France for its financial support



Ce projet est cofinancé par l'Union européenne avec le Fonds européen de développement régional

