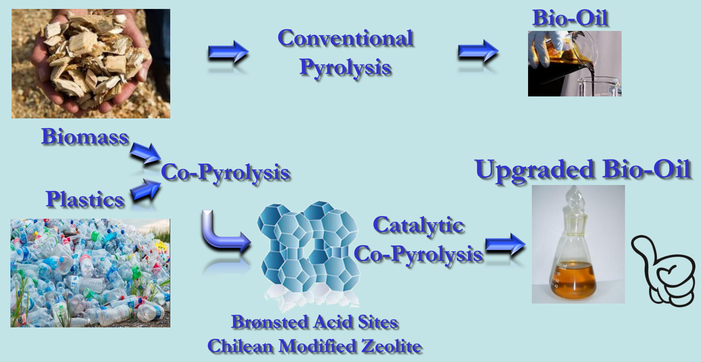
# CO-PYROLYSIS OF LOW-DENSITY POLYETHYLENE AND CHILEAN OAK USING NATURAL AND MODIFIED ZEOLITES: A Py-GC/MS STUDY

Serguei Alejandro-Martín[a,b], Francisco Medina Jofre[a]
[a]Laboratory of Gas Chromatography and Analytical Pyrolysis (LGCAP), Universidad del Bío-Bío, Concepción, Chile.
[b]Wood Engineering Dept., Fac. of Engineering, Universidad del Bío-Bío, Concepción, Chile.

## Introduction




## Objective

To investigate the chemical composition of evolved gas from analytical catalytic co-pyrolysis of Chilean Oak (ChO) and Low-Density Polyethylene (LDPE) using natural and modified Chilean zeolites as catalyst.

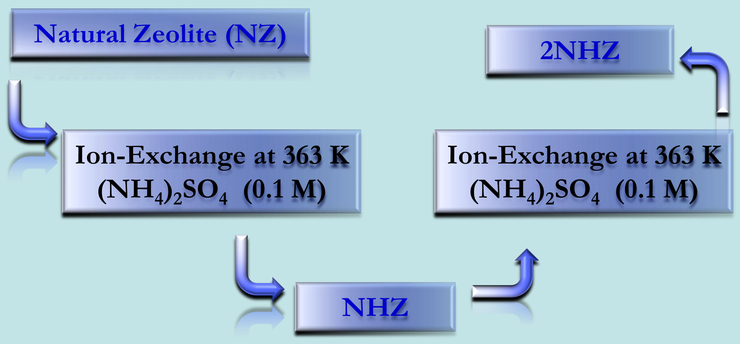
## Materials

Chilean natural zeolite (NZ) was provided by Minera FORMAS Ltd., Santiago, Chile. Low density polyethylene was donated by UDT-UDEC, Concepción, Chile. Biomass samples of Chilean Native Oak (*Nothofagus obliqua*) were obtained from a single tree, donated by Miraflores Angol Ltd., Chile.

## Methods

Chilean natural zeolites were ground and sieved to 0.3–0.425 mm, then rinsed with ultrapure water, oven-dried at 398 K for 24 h, and finally stored in a desiccator until chemical modification. Low density polyethylene (LDPE) was ground and sieved to 0.3–0.425 mm, then rinsed with ultrapure water, oven-dried at 313 K for 24 h. Chromatographic data registered from catalytic co-pyrolysis (ChO/LDPE) were processed using Turbo Mass software and mass spectra laboratory databases (NIST 2017 v2.3).

### Chemical modification of natural zeolites




Zeolite samples were characterized via nitrogen absorption at 77 K, XRD, XRF and pyridine adsorption followed by DRIFT. Oak samples were subjected to size reduction and characterized using the following standard methods: UNE-EN 14774, UNE-EN 14775, UNE-EN 14918, UNE-EN 15104 and ASTM D 3172-73(84).

### Experimental System

Pyrolysis experiments were conducted in a CDS Analytical Pyroprobe (5200 HPR), configuring a three-layer fixed bed (zeolite/ChO-LDPE/zeolite; separated by glass wool) in a quartz tube. First, the ChO/LDPE ratio was varied from 2:1, 1:1, and 1:2. Then, a ratio of 1/4 and 1/10 was used for (ChO/LDPE)/zeolite samples preparation. Finally, samples were pyrolysed by 15s at 550°C to generate the pyrolytic evolved gas stream. Gaseous chemical composition was analysed in a Perkin Elmer Gas Chromatograph (Clarus 690, Elite 1701 capillary column) coupled to a Mass Spectrometer (Clarus SQ8T) to analyse chemical composition.

## Results and Discussion

### 1.- Characterization of zeolite samples

| | ZN | NHZ1 |
|---|---|---|
| $S_{Lang}$ [m²/g] | 168.17 | 219.14 |
| $SiO_2$[a] | 71.61 | 75.27 |
| $Al_2O_3$[a] | 15.18 | 15.59 |
| $Na_2O$[a] | 2.00 | 0.46 |
| CaO[a] | 3.43 | 1.67 |
| $K_2O$[a] | 2.03 | 1.92 |
| MgO[a] | 0.74 | 0.60 |
| Si/Al | 4.71 | 4.83 |

[a] by X-ray fluorescence (% w/w)

Following the pyridine adsorption by a DRIFT technique allowed the identification of Brønsted and Lewis acid sites on natural and ammonium-modified zeolite, as shown in Figure 1.

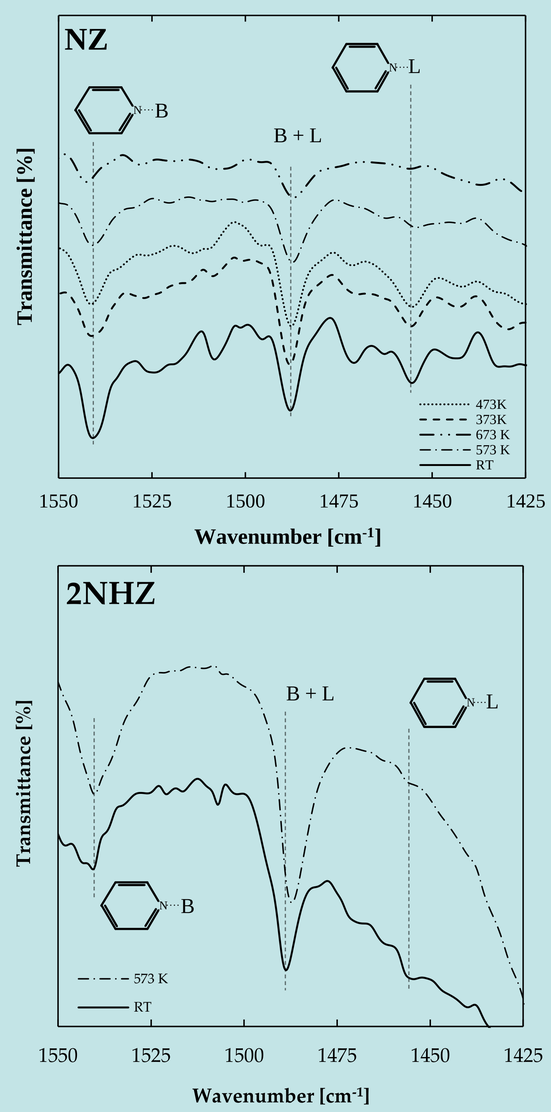



Figure 1. DRIFT spectra of adsorbed pyridine on zeolite samples.

Adsorbed pyridine on the Brønsted (Py-B) and Lewis (Py-L) acid sites were confirmed by the registered peaks near 1540 and 1450 cm−1, respectively. Based on the above, at least one Lewis acid site and one type of Brønsted site were confirmed. A progressive thermal desorption procedure was conducted to evaluate Brønsted and Lewis acid site strength.

Figure 1 shows collected spectra after the heating procedure applied to pyridine-saturated samples. A higher peak was registered at 1539 cm−1 for outgassed samples at 673 K, confirming the higher strength of Brønsted acid sites compared to Lewis acid sites. Thus, stronger Brønsted acid sites will cause bond breakage, transforming oxygenated compounds into other species. Stronger sites were needed here, considering that the C–O bond breakage limits the possibility of oxygenated compound removal. Brønsted acid sites are responsible for acid-catalysed reactions such as cracking, dimerisation, cyclisation and dehydrocyclisation.

### 2.- Characterization of Chilean Oak biomass

| Moisture [%w, d.b] | GCV [a] [MJ/Kg] | GCV [b] [MJ/Kg] | NCV [MJ/Kg] | Ash [%w, d.b] |
|---|---|---|---|---|
| 5.09 | 14.15 | 19.74 | 18.51 | 0.29 |

[a] as received [b] after drying (373K by 24 hrs) d.b: dry basis

### Ultimate and Elemental Analysis

| Hollocellulose | Cellulose | Lignin | Extractives | C | H | O | N |
|---|---|---|---|---|---|---|---|
| 5.09 | 14.15 | 19.74 | 18.51 | 47.3 | 6.36 | 46.34 | n.d |

*All results are expressed in weight percentage n.d: non detected

### Thermogravimetric Analysis

| $T_{onset}$ [K] | $T_1$ [K] | $T_m$ [K] | $\alpha_m$ | $DTG_m$ [mg/s] | $T_{offset}$ [K] | $\alpha_{offs}$ | %R |
|---|---|---|---|---|---|---|---|
| 476.3 | 575.9 | 628.8 | 0.59 | 0.010 | 668.4 | 0.84 | 13.87 |

### 3.- Chemical composition of evolved pyrolytic gas

A semi-quantitative GC/MS analysis of evolved gaseous stream was conducted to identify and group chemical species by compound families.

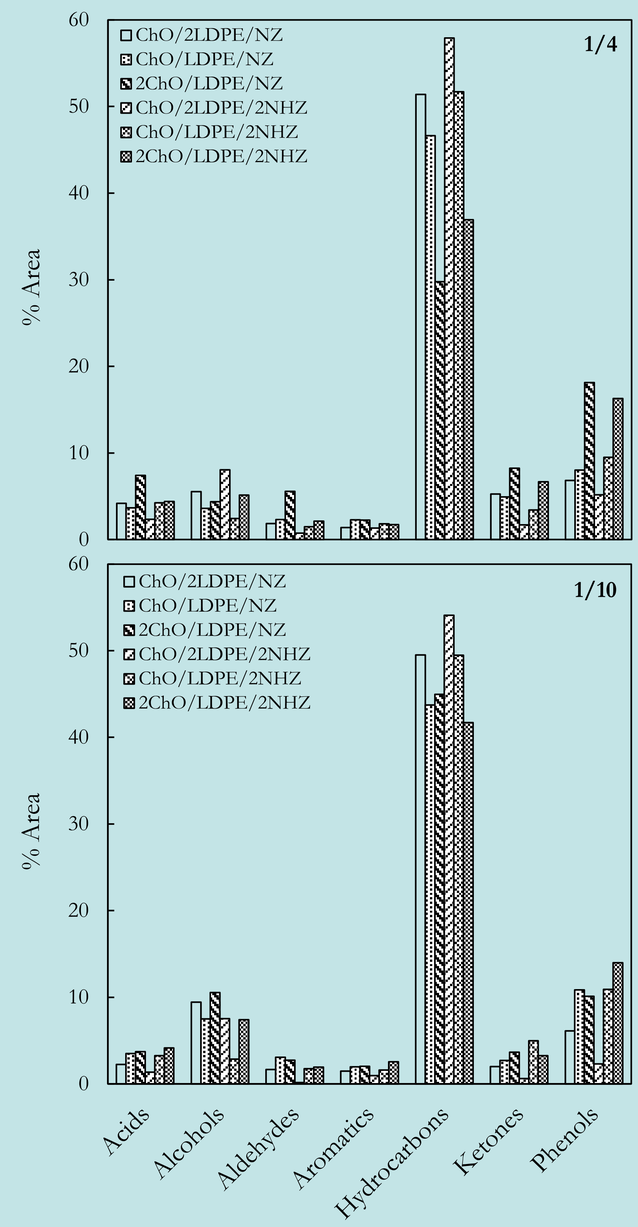



Figure 2. Leading compounds families in evolved pyrolytic gas at different ChO/LDPE ratio (1/4 and 1/10).

## Conclusions

Results showed the contribution of natural and modified zeolites during co-pyrolysis of Chilean Oak and LDPE at 550°C. Thus, the selectivity toward hydrocarbons was enhanced when biomass was combined with LDPE. On the other hand, phenol production was reduced during co-pyrolysis compared with the pyrolysis of Chilean Oak.

Furthermore, when ammonium-modified zeolite was used, the hydrocarbon composition was higher than those obtained with natural zeolite. Therefore, Chilean natural zeolites can be an alternative catalyst for getting value-added chemicals and valorising plastic and lignocellulosic residues through co-pyrolysis.

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**Contact:**
Serguei Alejandro-Martín, Ph.D.
Laboratory of Gas Chromatography and Analytical Pyrolysis (LGCAP)
Wood Engineering Department. University of Bio-Bio, Concepción, Chile
Tel.: 56 41 311 1168 e-mail: salejandro@ubiobio.cl