IMPROVEMENT OF THE PRODUCTION OF AROMATIC COMPOUNDS OBTAINED FROM THE PYROLYSIS OF SCRAP TIRE RUBBER USING HETEROPOLYACIDS-BASED CATALYSTS

By

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Introducción

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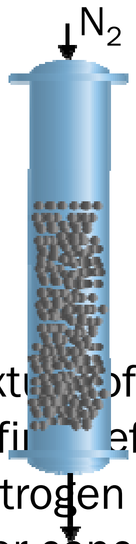
PYROLYSIS



Gas

Mixture of aromatics, paraffin, olefin and, sulfur and nitrogen compounds in lower concentrations[2]

D,L limonene 30-40 wt% [3]

BTX aromatics 6-8 wt%[3]

Benzene
Toluene
Xylenes
Ethylbenzene

Chemical synthesis of plastics, synthetic rubber, paints, pigments, explosives, pesticides, fragrances, degreasers and cleaning products. [4]

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[2] M. Rofiqul Islam, H. Haniu, M. Rafiqul Alam Beg, Fuel. 87 (2008) 3112–3122. [3] J.D. Martínez, M. Lapuerta, R. García-Contreras, R. Murillo, T. García, Energy and Fuels. 27 (2013) 3296–3305. [4] A. Rauter, F. Brito, J. Justino, M.E. Araújo, P. dos S. Susana, Natural Products in the New Millennium: Prospects and Industrial Application, 2013.

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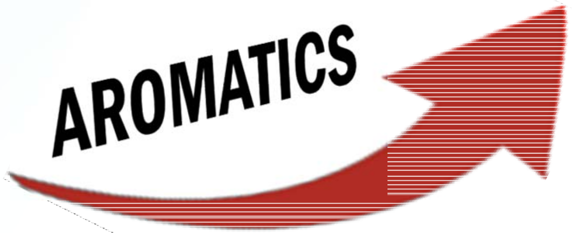

Zeolites | Bifunctional | Pure Silica

- Lower Si/Al ratio increase in the concentration of single ring aromatic compounds
- Decrease of oil yield and an increase of gas yield
- High cracking activity

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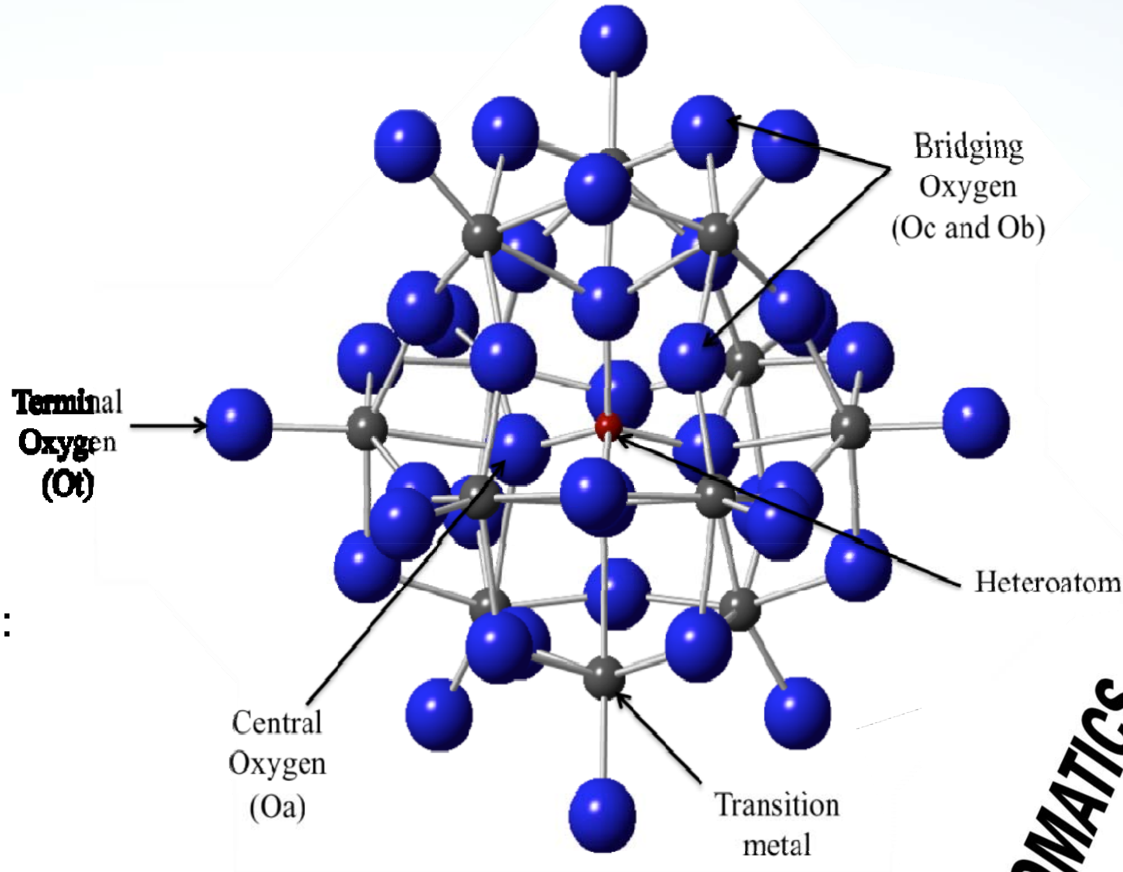
Introducción

NEW ALTERNATIVE

- Acid and redox functions
- Lewis and Brønsted acidity

Different reactions:

- Oxidation.
- Reduction.
- Condensation.
- Carboxylation.
- Dehydrogenation.
- Isomerization



HETEROPOLYACIDS

AROMATICS

P.T. Williams, A.J. Brindle, J. Anal. Appl. Pyrolysis. 67 (2003) 143–164. M. Olazar, R. Aguado, M. Arabiourrutia, G. Lopez, A. Barona, J. Bilbao, Energy and Fuels. 22 (2008) 2909–2916.

Methodology

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Pyrolysis of scr... rubber for the produ... imple ring a...

$H_4PMo_{11}VO_{40}$ (HPMoV)

1

$H_3PMo_{12}O_{40}$ (HPMo)

Optin... scrap tire rubber pyrolysis without catalyst

20 wt% on commercial silica CARiACT Q-10

2

$H_3PW_{12}O_{40}$ (HPW)

Pyrolysis of scrap tire rubber with catalytic stage

Wet impregnation

D_p= 0.85 - 1mm

Compound	Concentration (wt%)**
NR	50.05 ± 2.07
SBR	1.44 ± 0.125
BR*	14.72 ± 2.195
Black carbon + additives	33.79

Note: *It was determined by difference.
**Dry basis.

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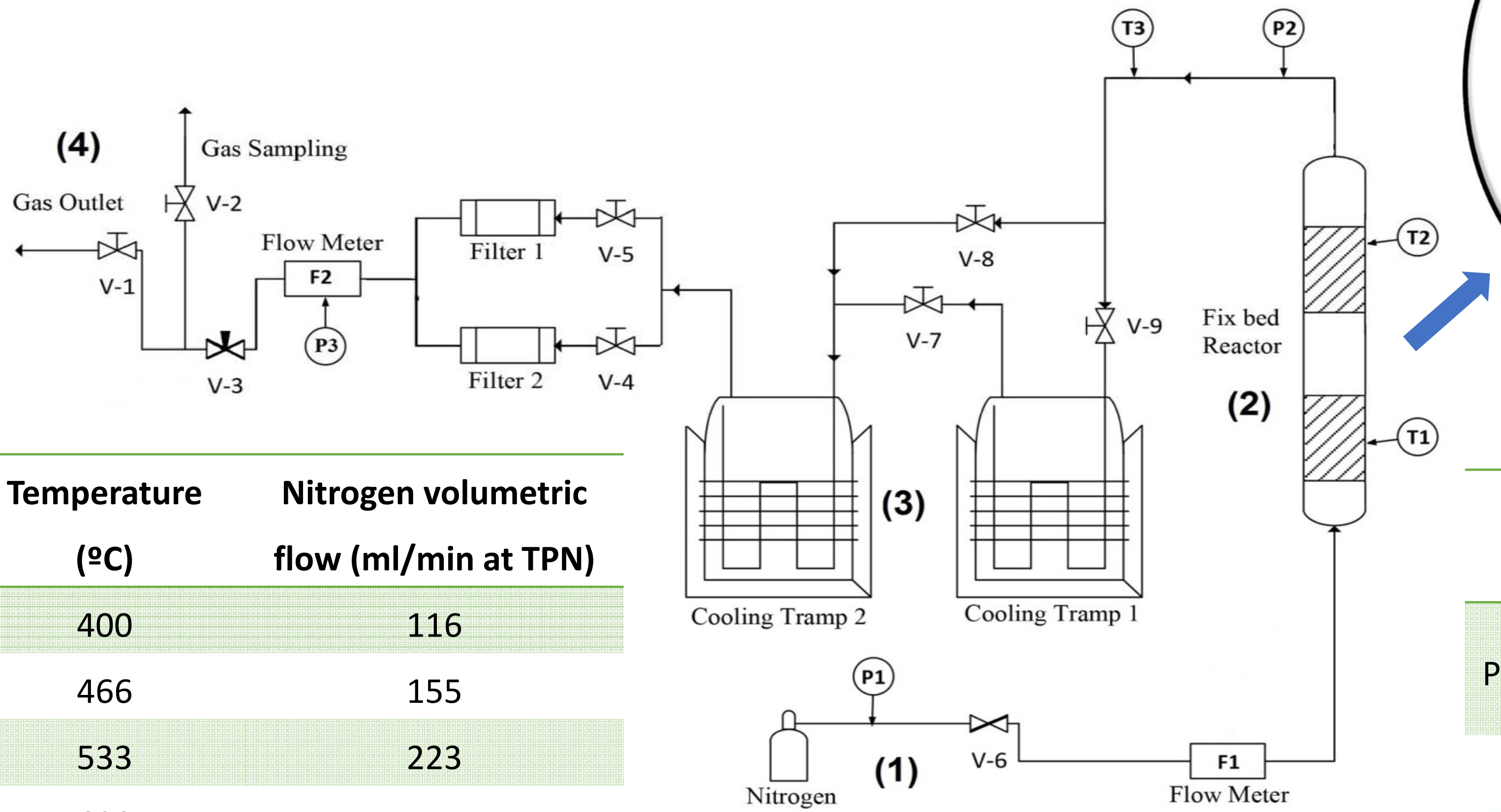
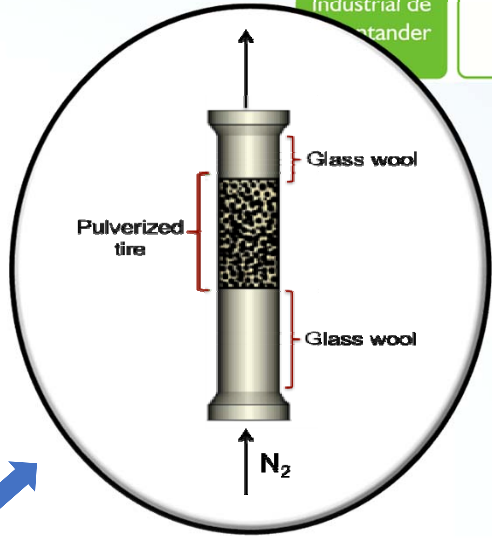
Methodology

1 Optimization of scrap tire rubber pyrolysis without catalyst



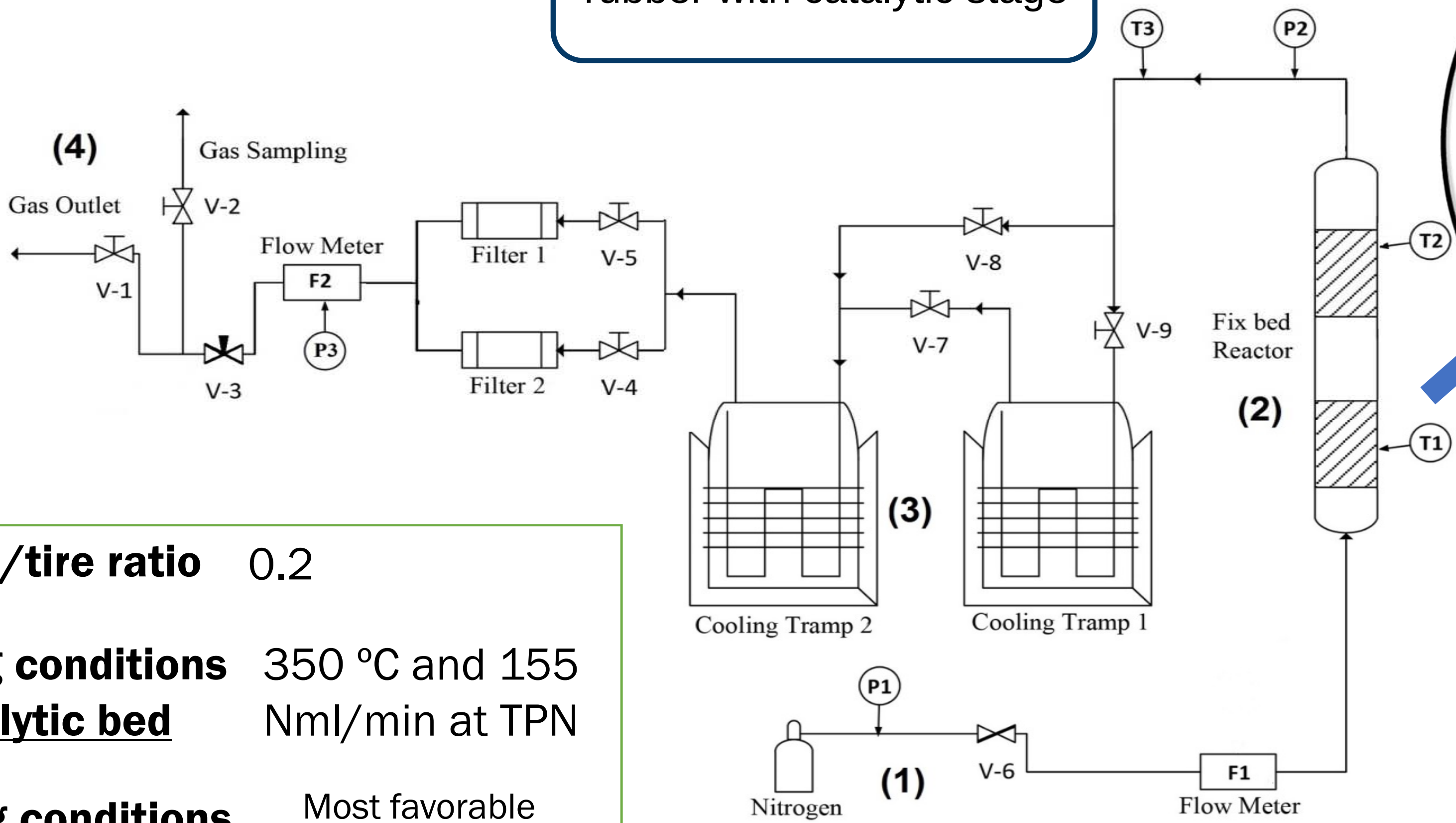


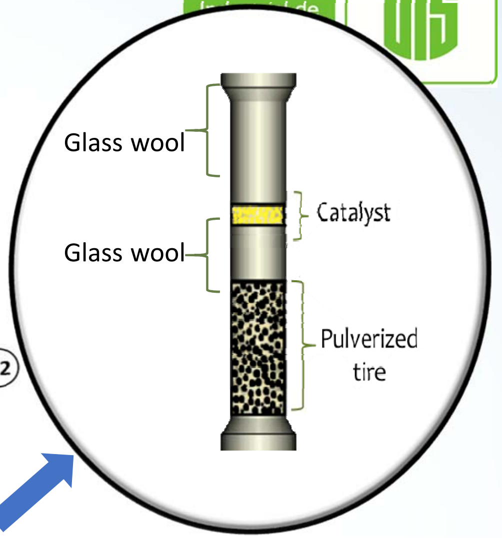
Temperature (ºC)	Nitrogen volumetric flow (ml/min at TPN)
400	116
466	155
533	223
600	

Response variable 1	Response variable 2
Pyrolytic oil yield	Aromatic compounds yield
(wt %)	(wt%)

Methodology

2 Pyrolysis of scrap tire rubber with catalytic stage





Catalyst/tire ratio	0.2
Operating conditions of catalytic bed	350 °C and 155 Nml/min at TPN
Operating conditions of scrap tire bed	Most favorable operating conditions found in stage 1

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Results and discussion

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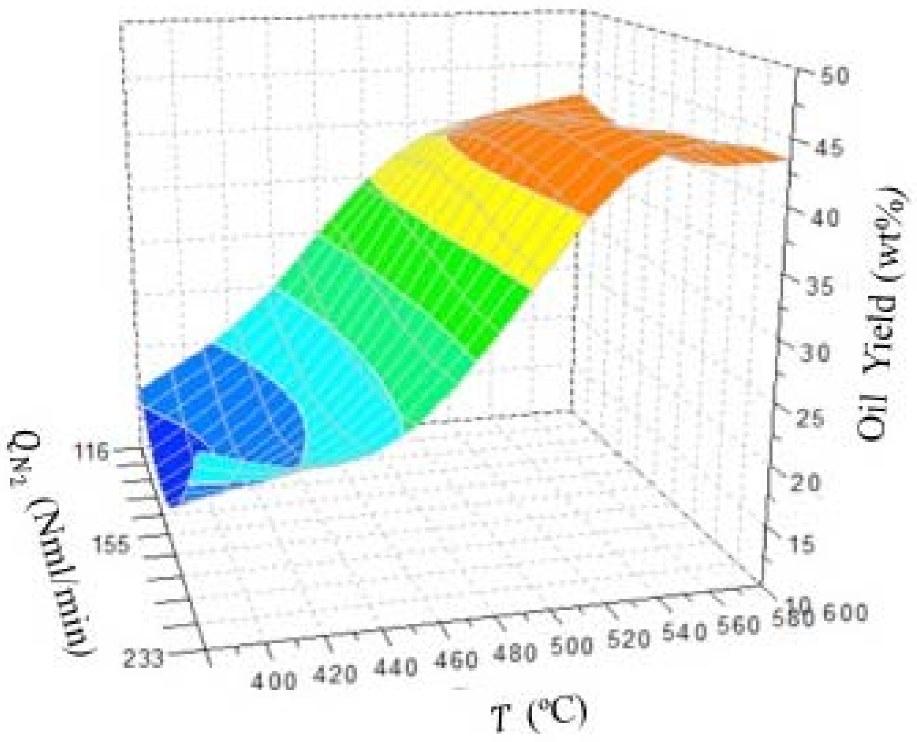
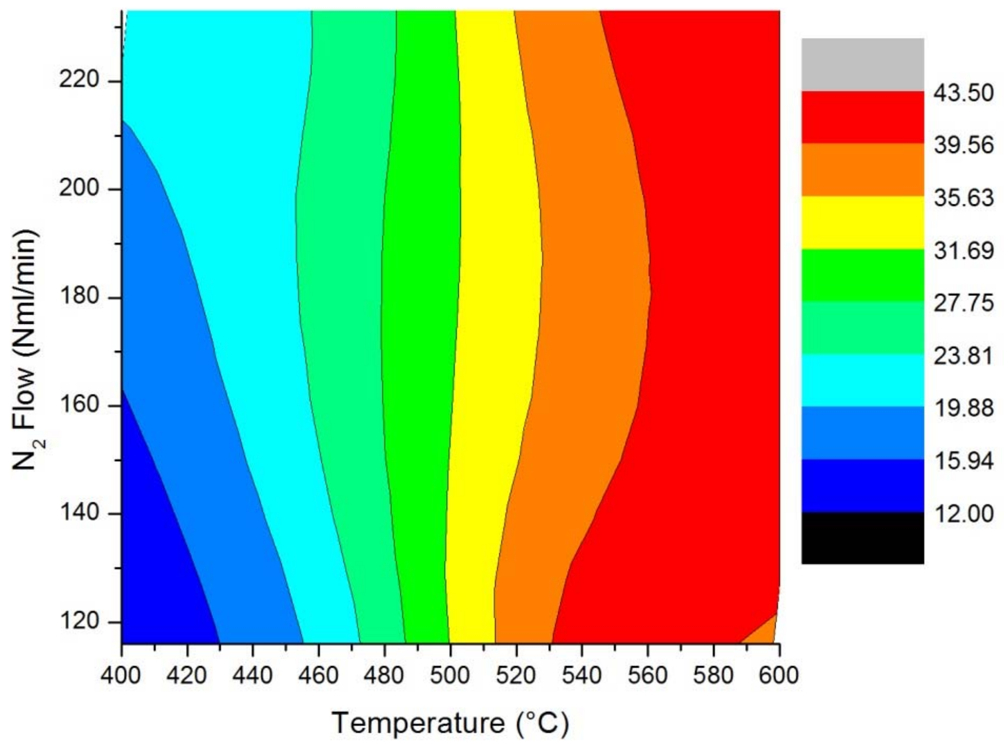
MAXIMUM OIL YIELD





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[2] M. Rofiqul Islam, H. Haniu, M. Rafiqul Alam Beg, Fuel. 87 (2008) 3112–3122. [5]H. Aydin, C. Ilkiliç, Fuel. 102 (2012) 605–612. [6] M. Banar, V. Akyildiz, A. Özkan, Z. Çokaygil, Ö. Onay, Energy Convers. Manag. 62 (2012) 22–30. [7] C. Berrueco, E. Esperanza, F.J. Mastral, J. Ceamanos, P. García-Bacaicoa, J. Anal. Appl. Pyrolysis. 74 (2005) 245–253. [8] C. Díez, M.E. Sánchez, P. Haxaire, O. Martínez, A. Morán, J. Anal. Appl. Pyrolysis. 74 (2005) 254–258. [9] I. De Marco Rodriguez, M.F. Laresgoiti, M.A. Cabrero, A. Torres, M.J. Chomón, B. Caballero, Fuel Process. Technol. 72 (2001) 9–22.

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Results and discussion

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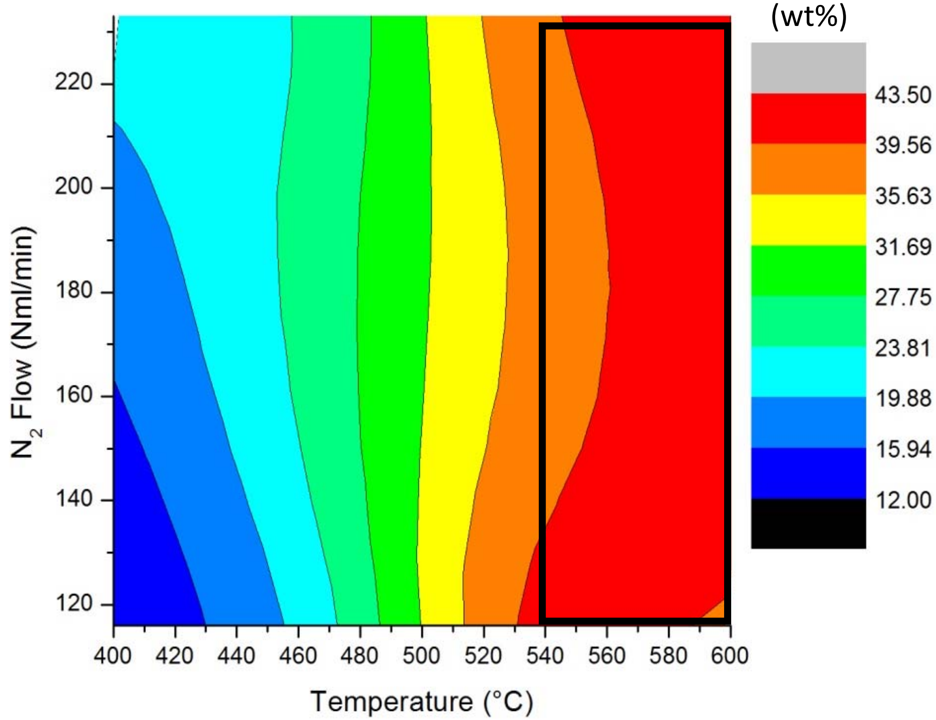
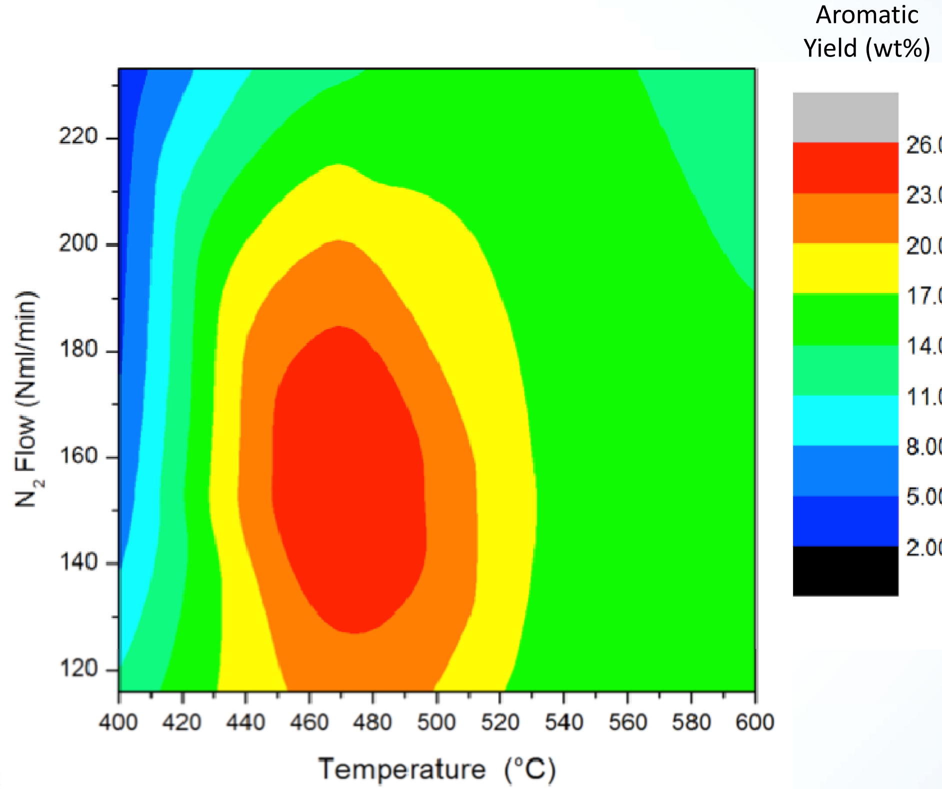
MAXIMUM AROMATIC YIELD

MAXIMUM OIL YIELD





600 ºC and 233 Nml/min ≠ 466 ºC and 155 Nml/min

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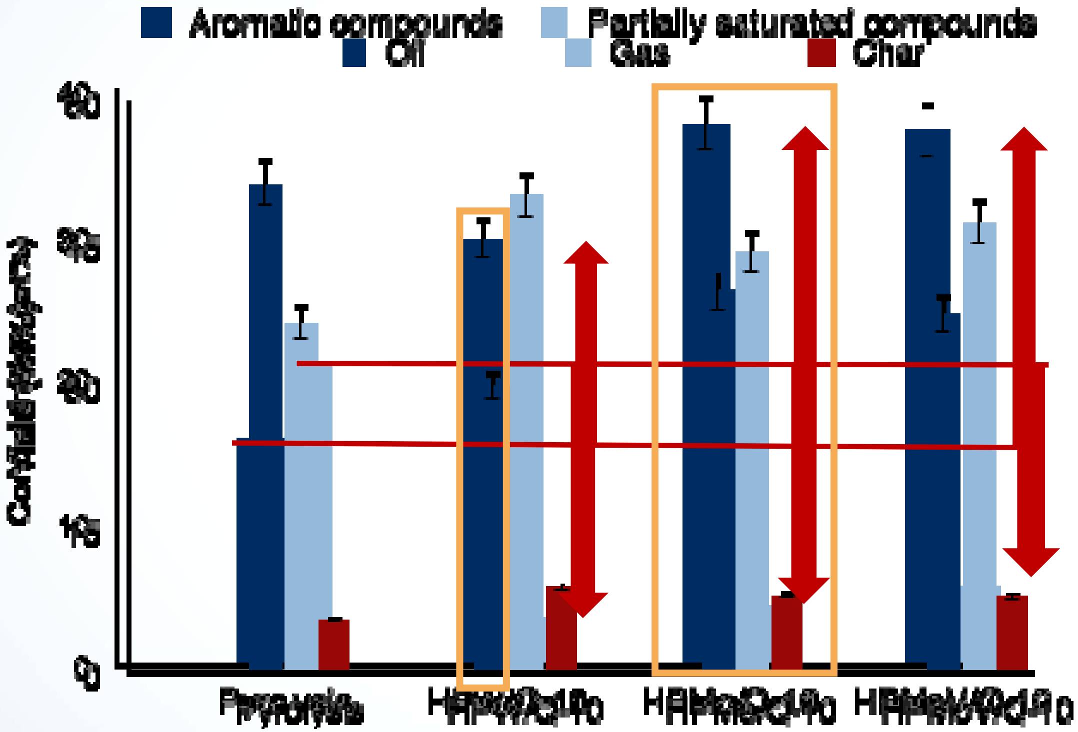
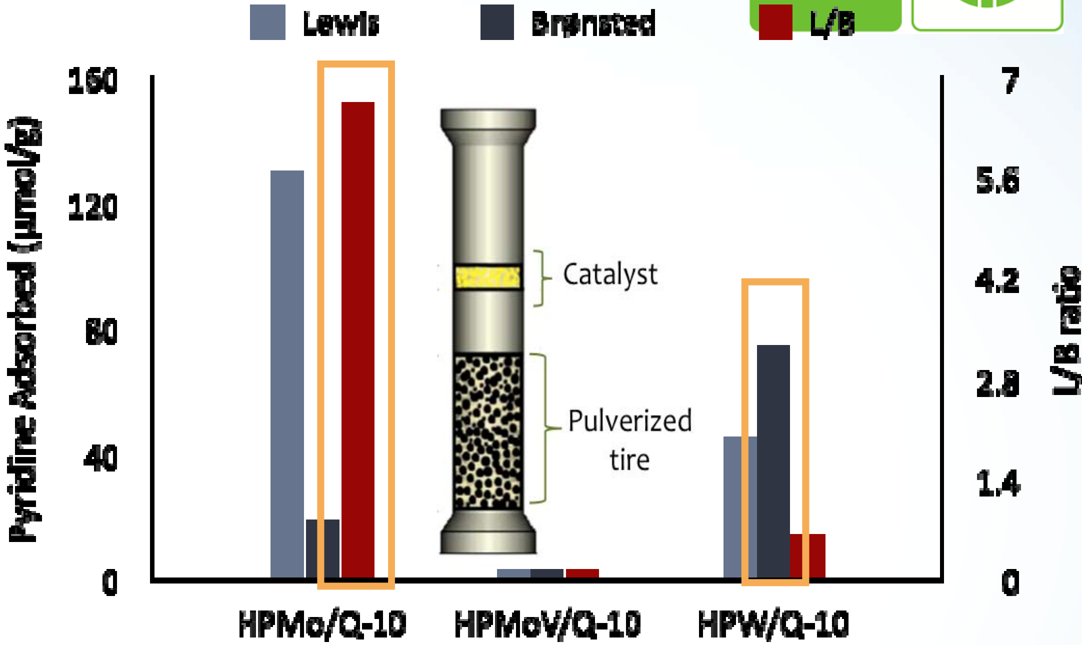
Products yields obtained with the pyrolysis with and without catalytic step

Aromatic concentration in oil with the pyrolysis with and without catalytic step

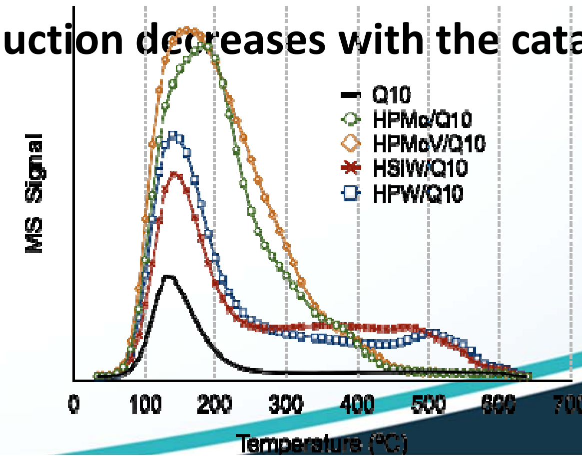


Brønsted Acidity = Increase gas yield

Cracking reactions



The oil production decreases with the catalysts



Results and discussion

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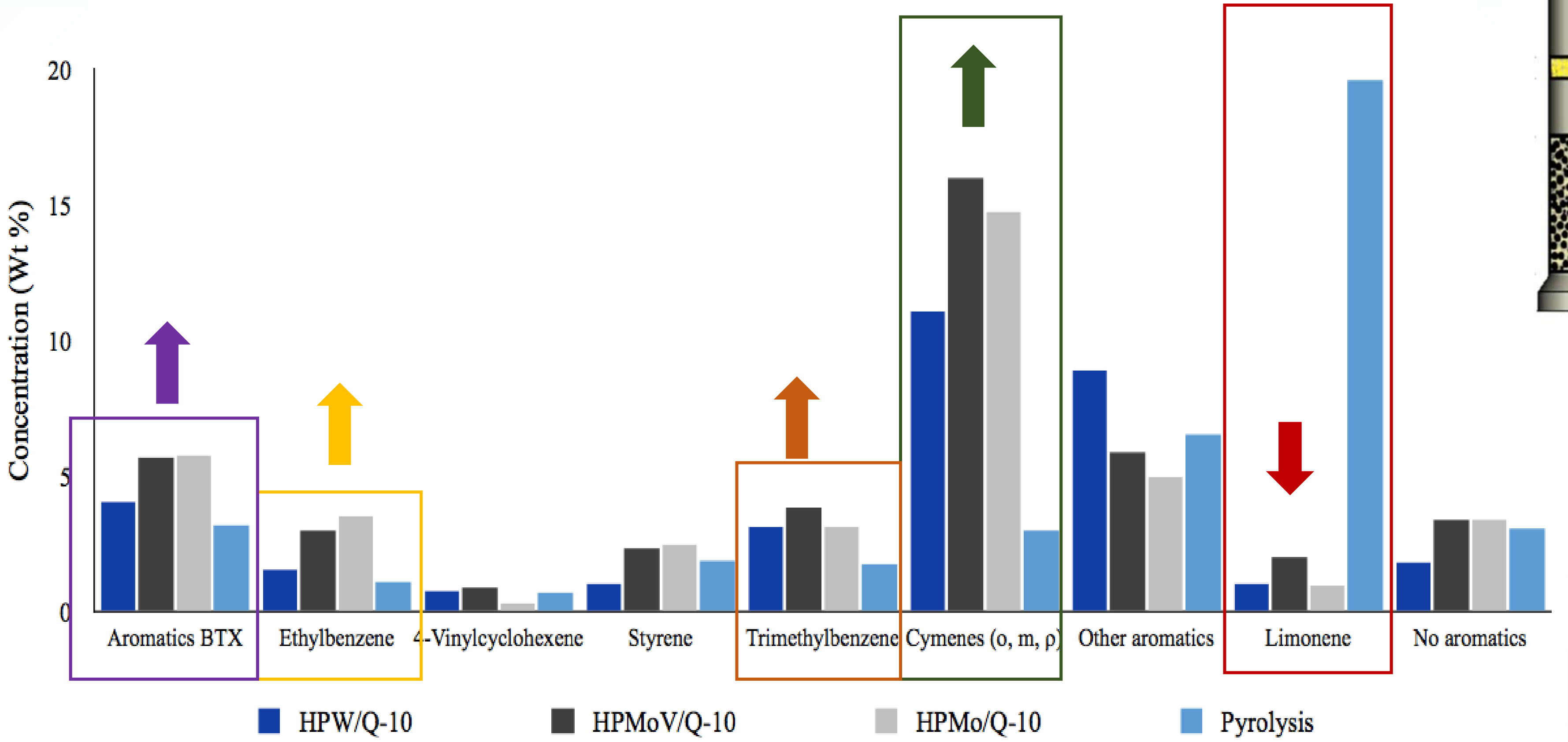
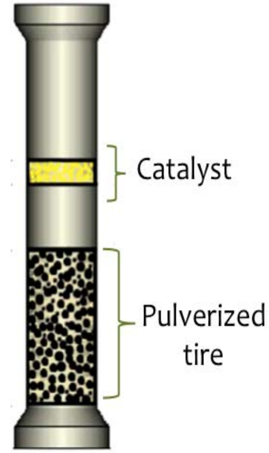
Concentration of the aromatics and the partially saturated cyclic compounds in the pyrolytic oil





Conclusions

- ✓ The operating variables for the pyrolysis of scrap tires having the most influence on distribution of products are the.

  The highest yield of pyrolysis oil does not necessarily lead to a higher yield of aromatics.

- ✓ The HPA based catalysts used in the catalytic reforming of volatiles from STR pyrolysis allow increasing the production of aromatic compounds but decrease the pyrolytic oil yield.

- ✓ The number of Brønsted sites do not promote the oil yield, founding in this study a decrease up to 41% when the Tungsten-based catalyst was used. Therefore, the gas yield was slightly increased.

Conclusions

- ✓ On the contrary, the aromatic concentration in pyrolytic oil was increased to close to 140% when Molybdenum-based catalysts were used. Conversely, at these conditions, the concentration of partially saturated cyclic compounds, such as limonene, was drastically decreased.

- ✓ Cymenes compounds were the major aromatic compounds in pyrolytic oil as a result of the reforming of D, L limonene. The results show that the Molybdenum-based catalysts with an high ratio of Lewis/Brønsted acid sites favors its production

THANK YOU FOR YOUR ATTENTION

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