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Green aromatic bulk-chemicals from lignin pyrolysis vapours

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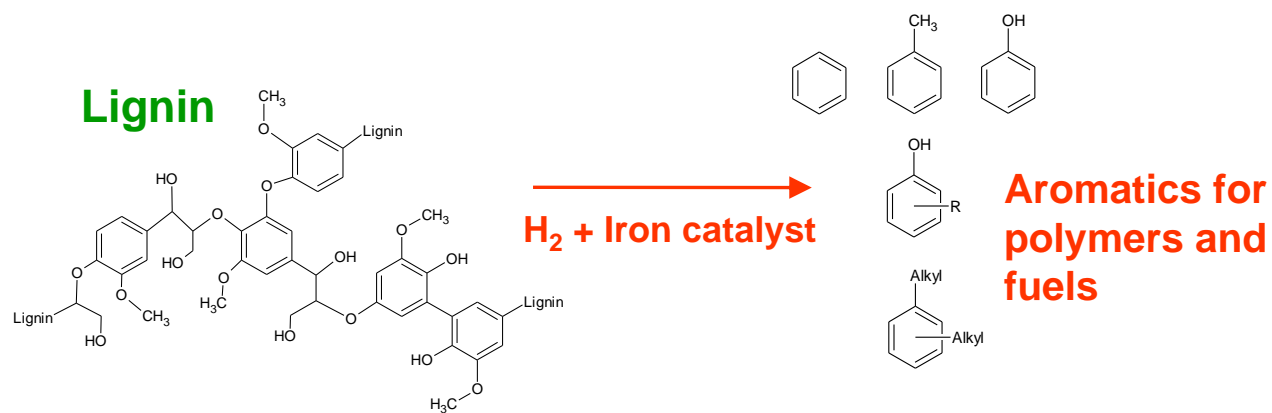
Authors

B. Shrestha, R. Olcese, J. Francois, M. Bettahar, D. Petitjean, and A. Dufour

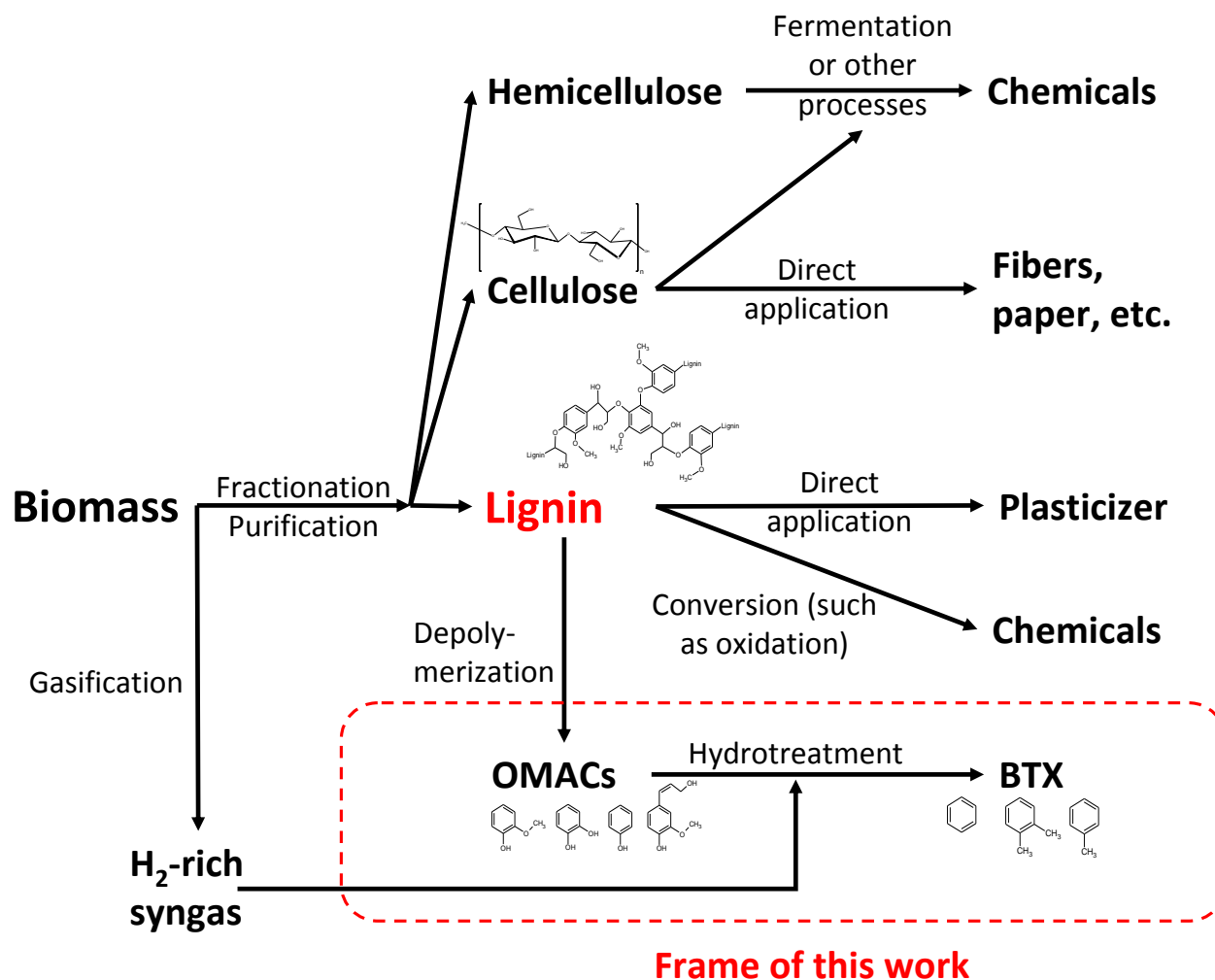
Green aromatic bulk-chemicals from lignin pyrolysis vapours

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M. Bettahar, D. Petitjean, A. Dufour

CNRS, Université de Lorraine

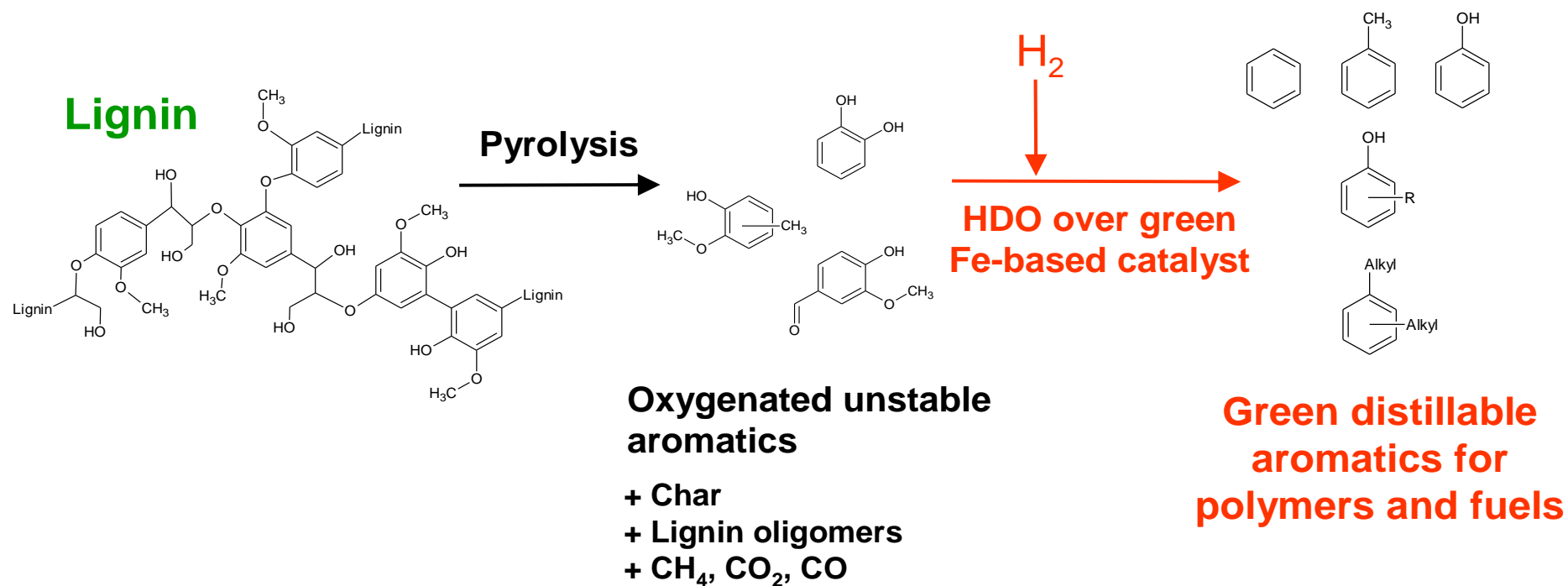


The production of aromatics from lignin is an important challenge for biorefinery

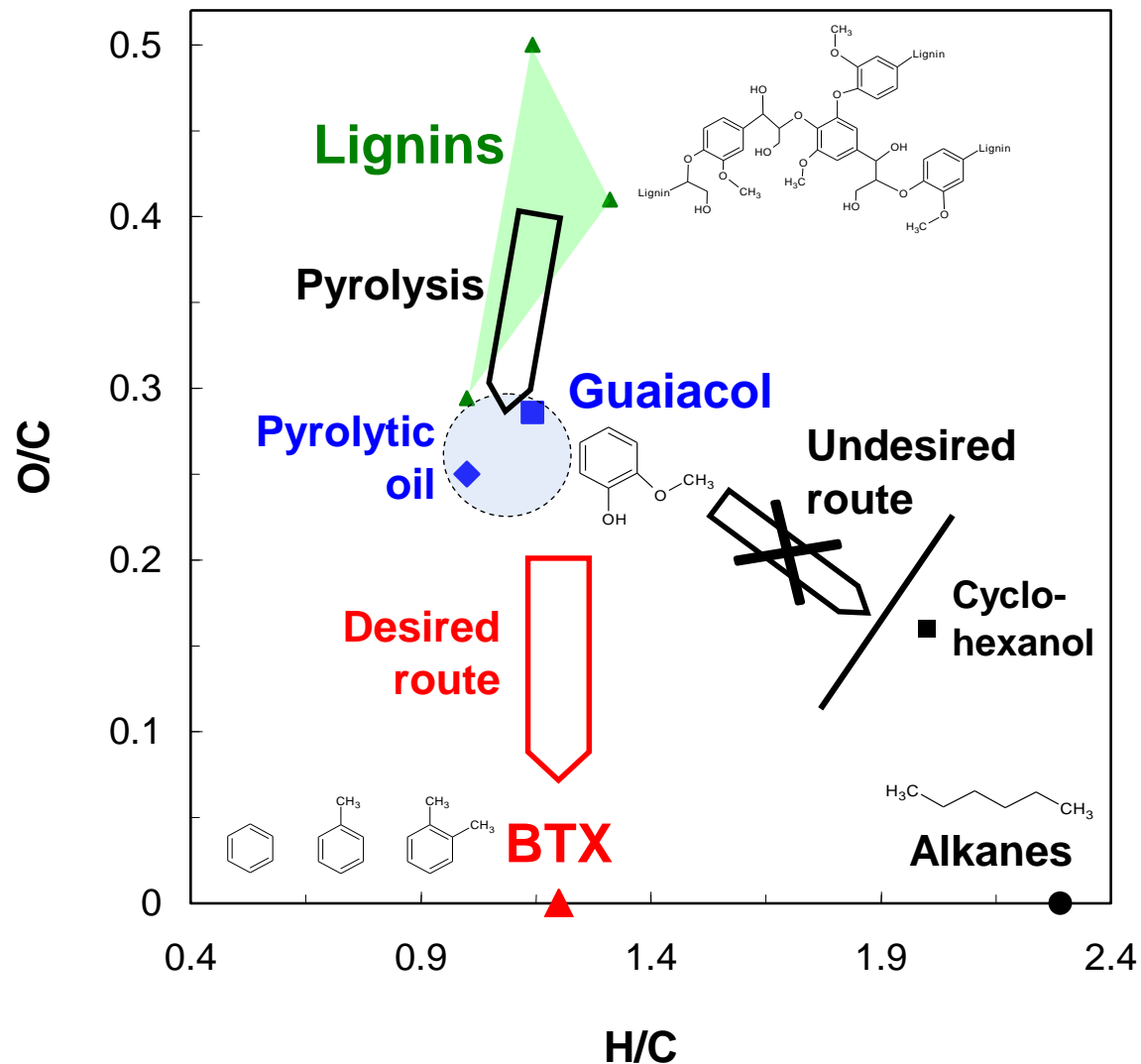


OMACs = Oxygenated Mono Aromatics Compounds

Aromatics could be produced by gas-phase hydrodeoxygenation (HDO) of pyrolysis vapours

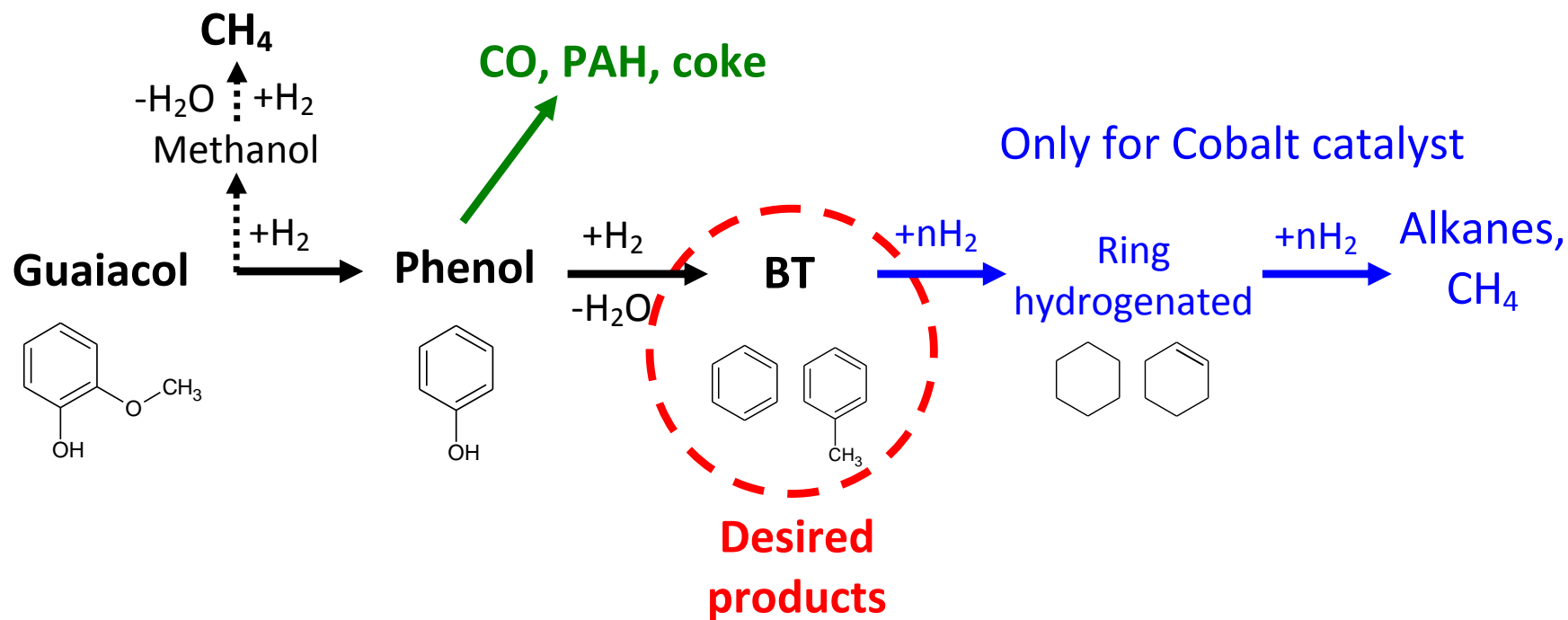


A green and cheap catalyst is looked for a selective HDO of oxygenated pyrolysis products

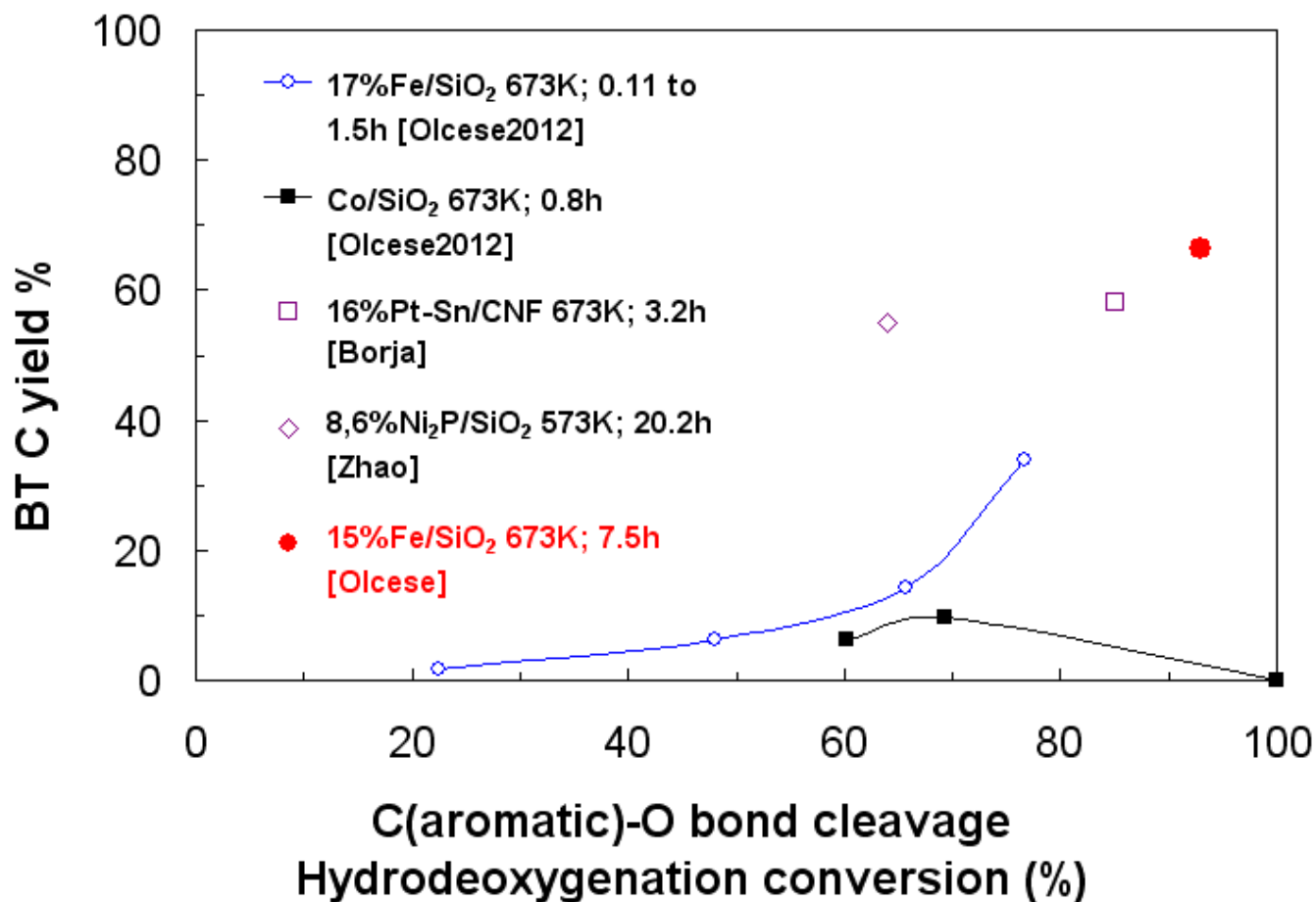


Olcese et al.
App. Catal. B.
115 (2012) 63

The HDO of guaiacol, a surrogate of pyrolysis products, has been studied over iron-based catalysts.

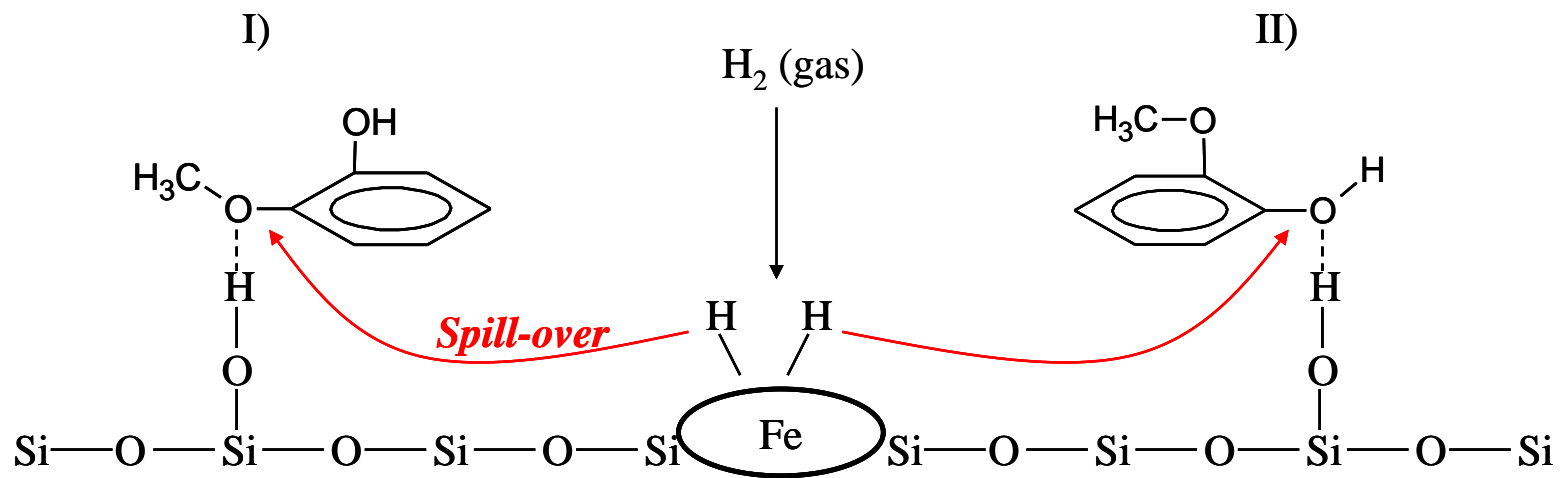


Fe/SiO₂ is a selective catalyst for the HDO of guaiacol into benzene and toluene



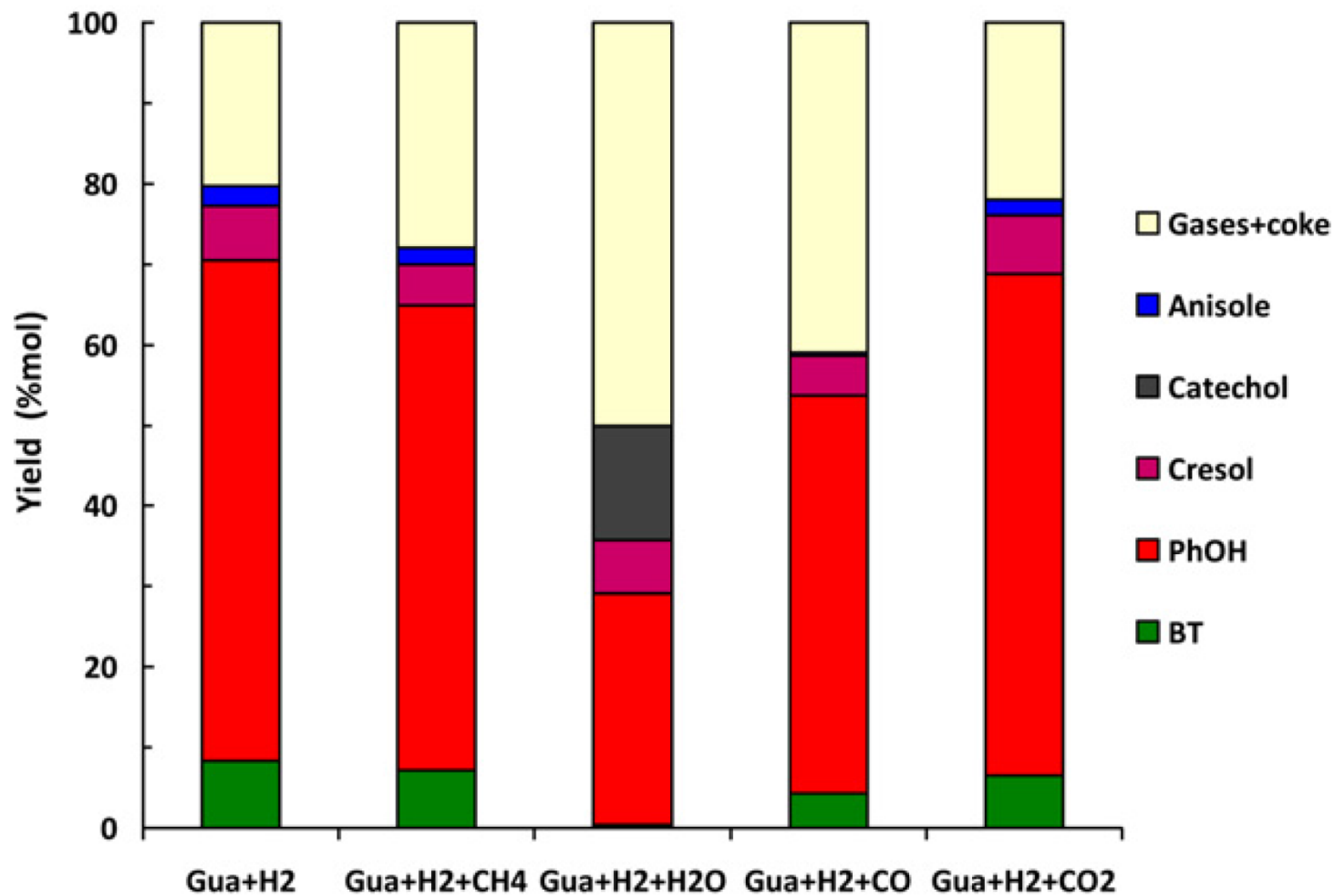
Mass residence time= 1/WHSV = g catalyst/(g guaiacol/h)

Catalytic mechanism of guaiacol HDO over Fe/SiO₂



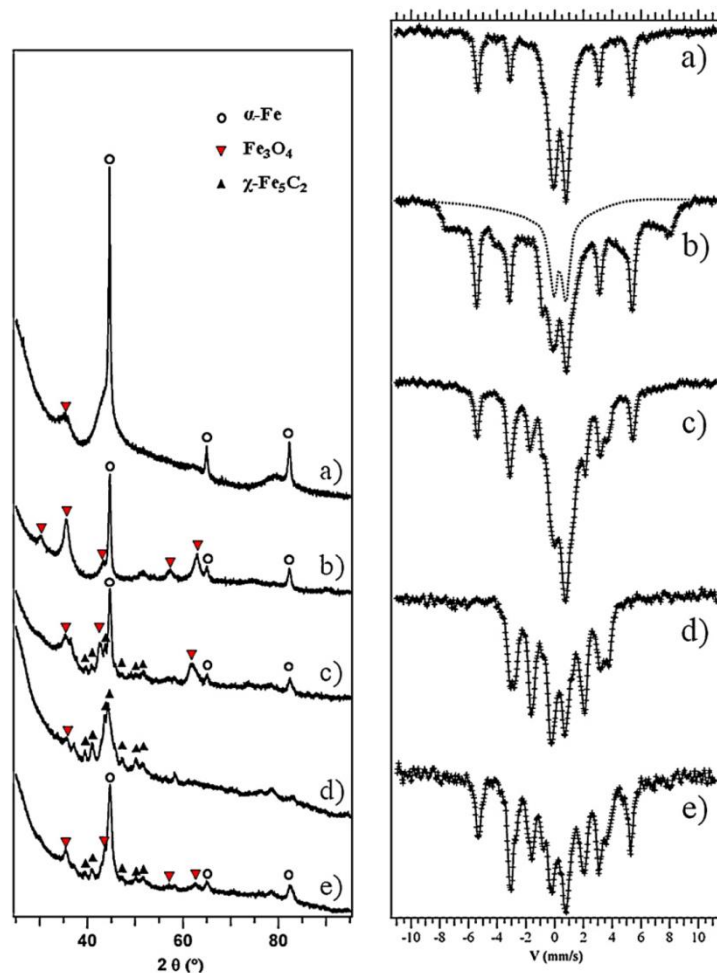
Olcese et al. App. Catal. B. 116 (2012) 63-73

Gas composition has an effect on selectivity

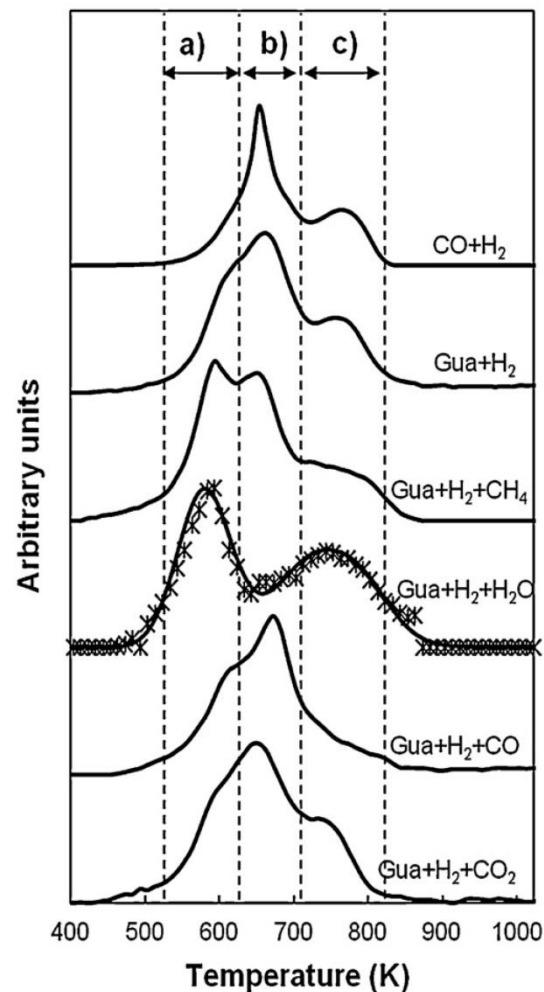


Gas composition has an effect on iron speciation and on « coke » composition

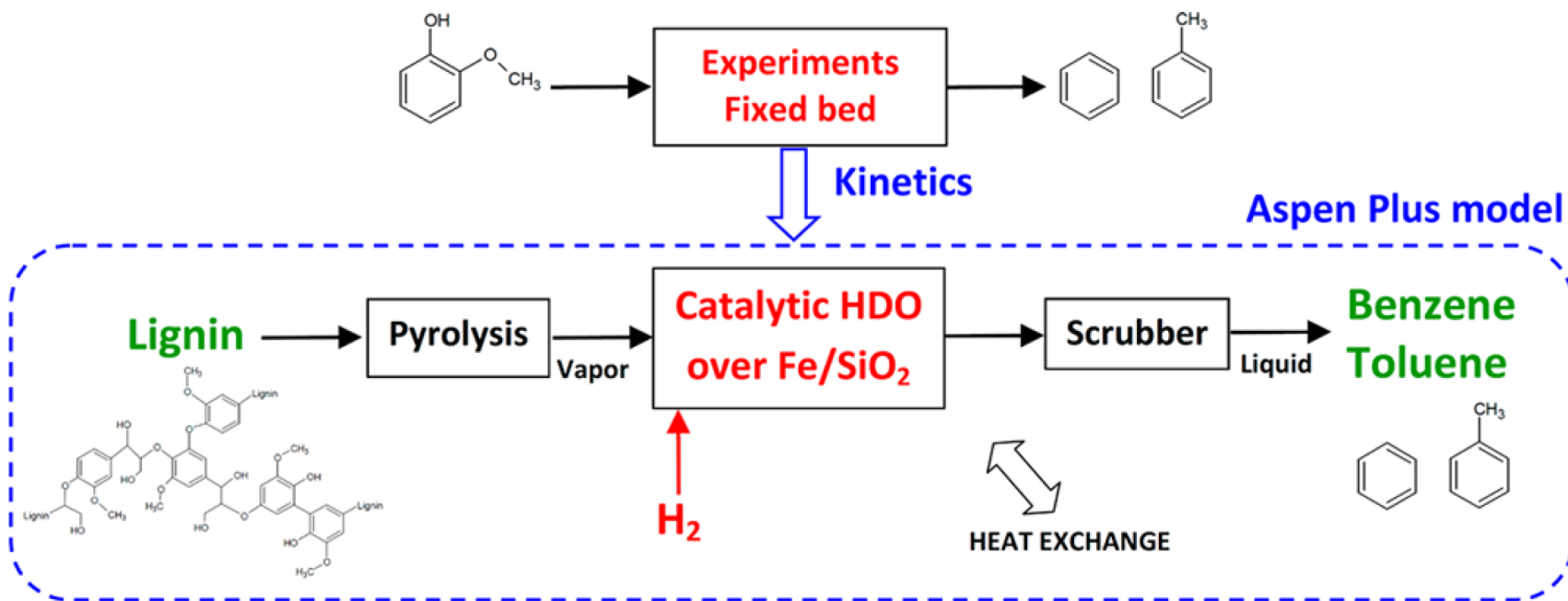
Iron speciation analysed by XRD & Mössbauer



Coke analysed by Temperature Programmed Oxidation

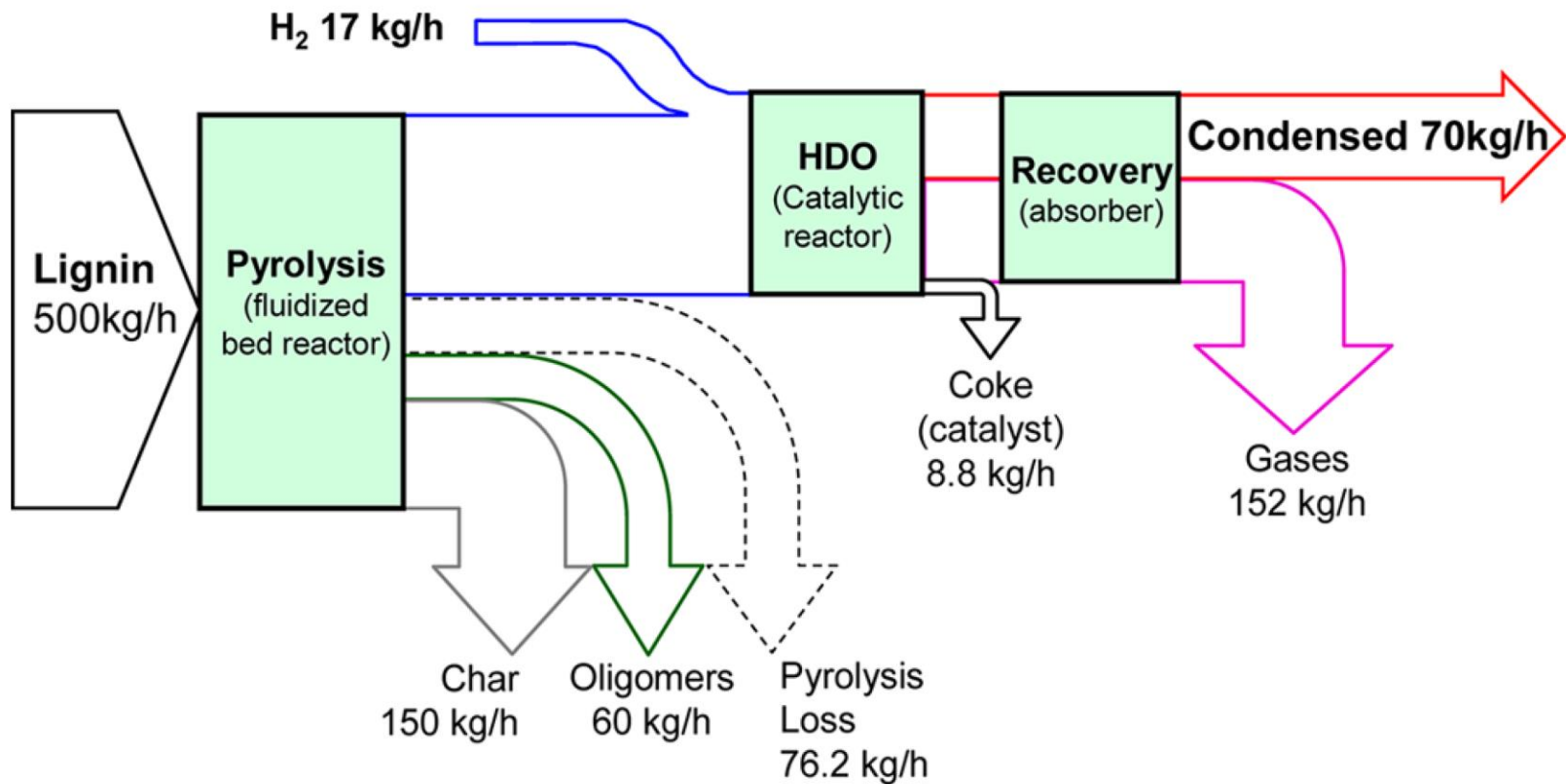


A kinetic model has been developed and included under Aspen Plus for process modeling



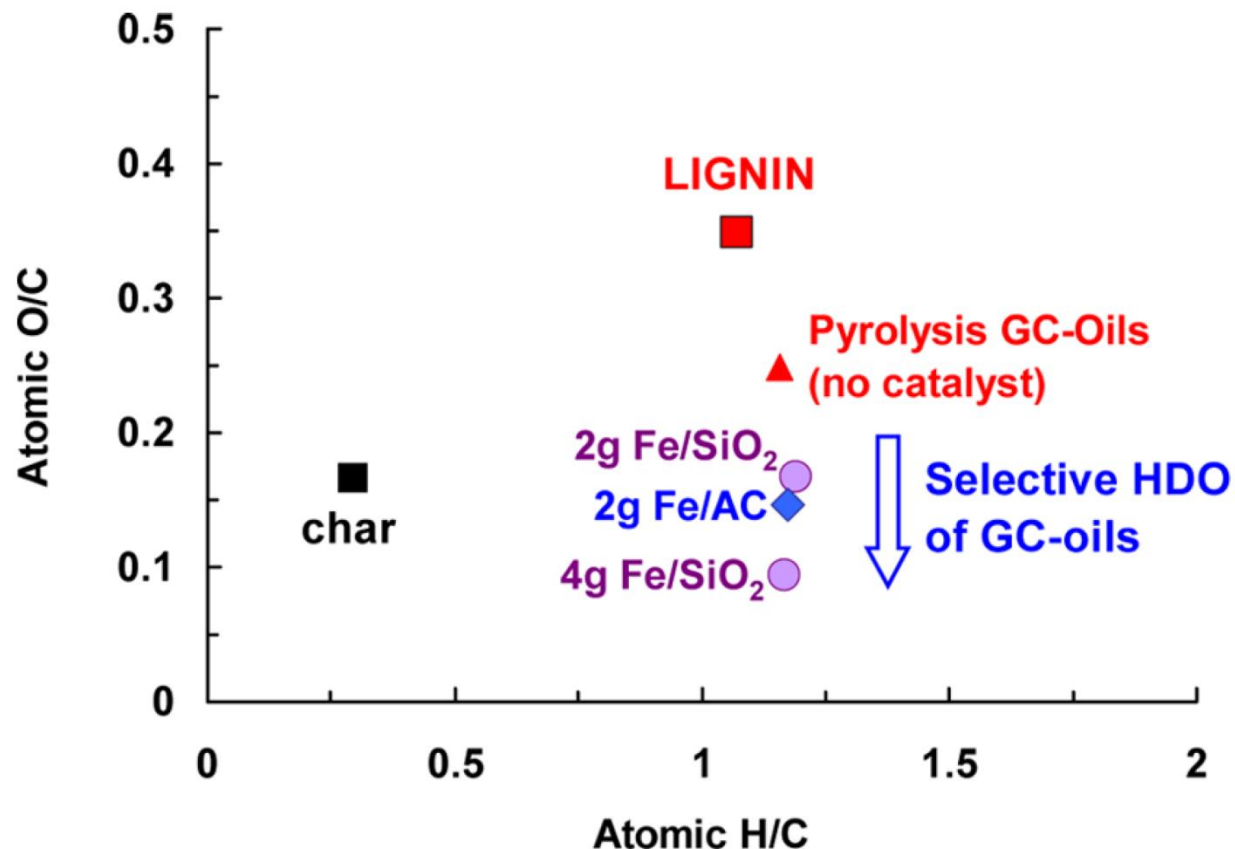
Olcese et al. Energy Fuels 27 (2013) 975

Mass balance of the whole lignin to BTX process is modeled

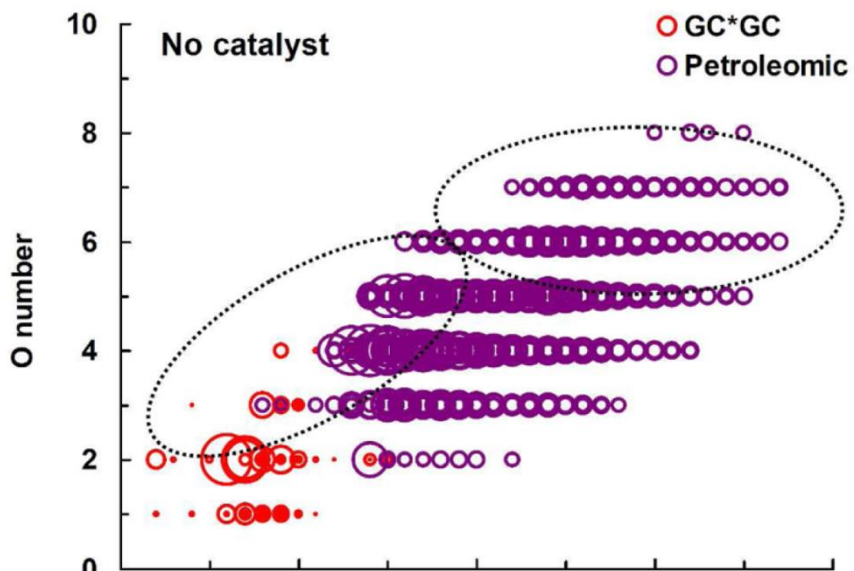


Char and oligomers represent a key issue to improve lignin conversion yields into aromatics

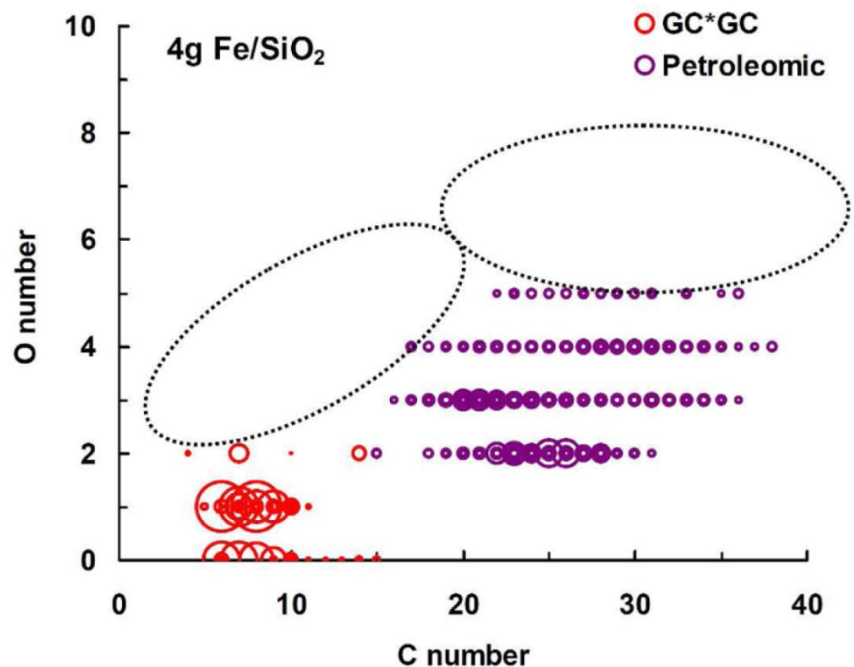
Experiments have also been conducted on REAL pyrolysis vapours



A selective HDO has been obtained by iron-based catalysts

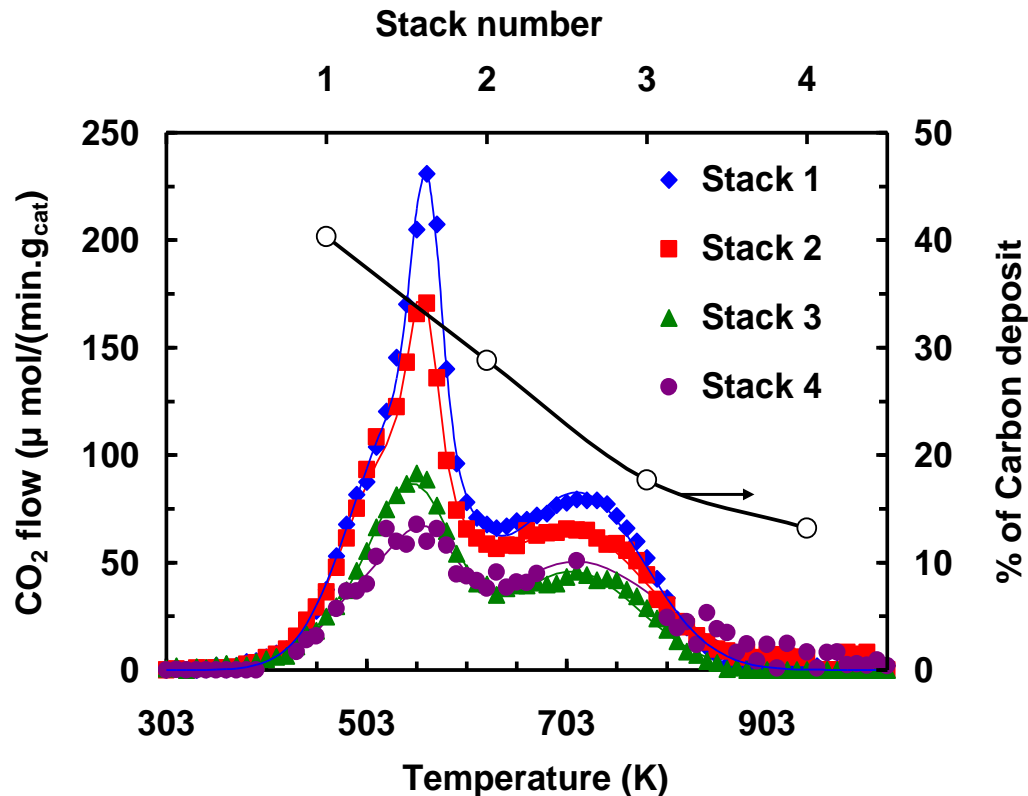


GC*GC and high resolution mass spectrometry (« Petroleomic ») are complementary methods



GC for light, petroleomic for heavier species

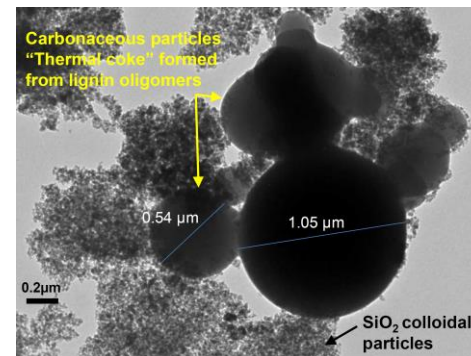
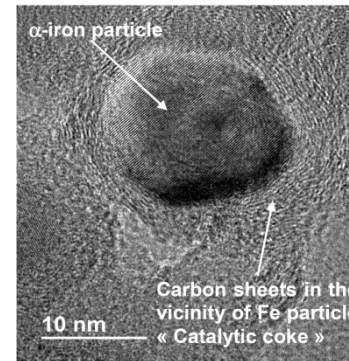
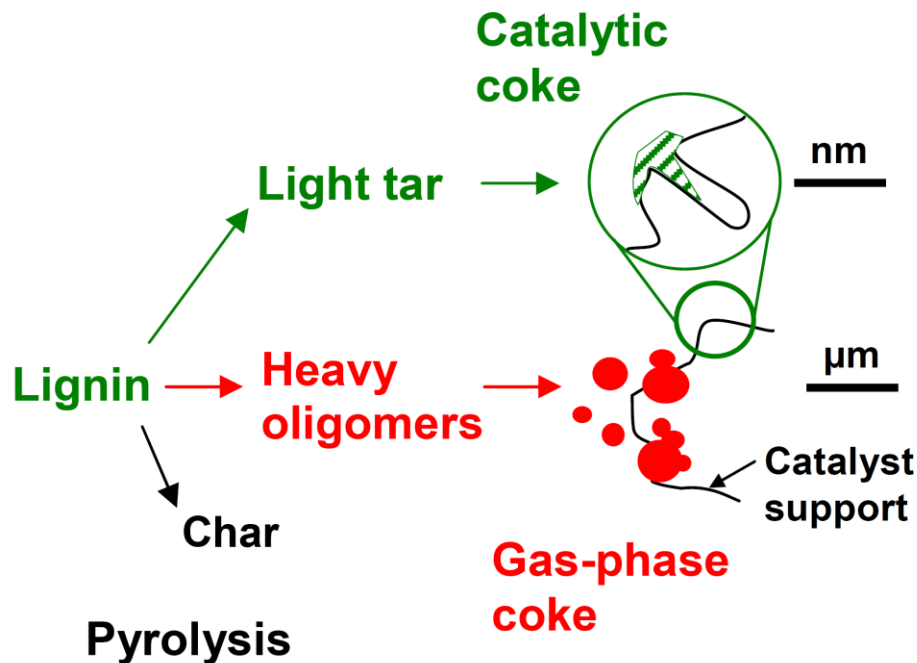
Coke formed by real lignin vapours is very different than coke from guaiacol HDO



Coke analysed along the length of the fixed bed (profile in coke composition)

Coke plugged micropores of activated carbon but not mesopores of silica

The mechanism of coke formation during the HDO of real vapours has been revealed



TEM, TPO, Petroleomic, GC*GC, N₂ sorption (etc.) were used to reveal this mechanism

Olcese et al. ChemSusChem, in press

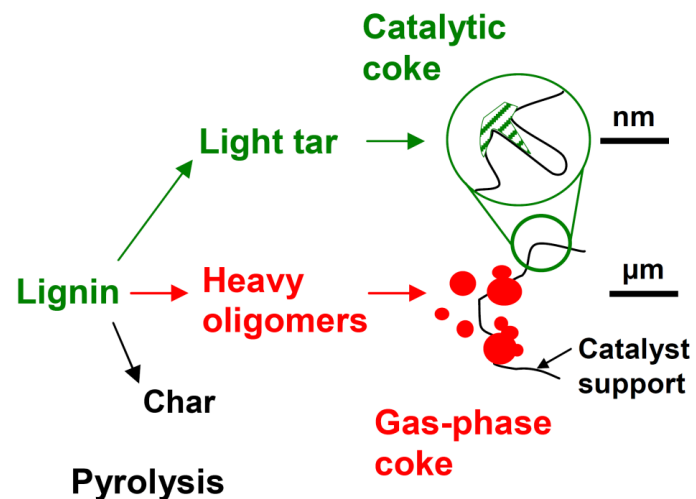
Iron is a selective and cheap catalyst for the HDO of lignin into aromatics

Works are conducted from molecular mechanisms to process integration

Thank you for your attention

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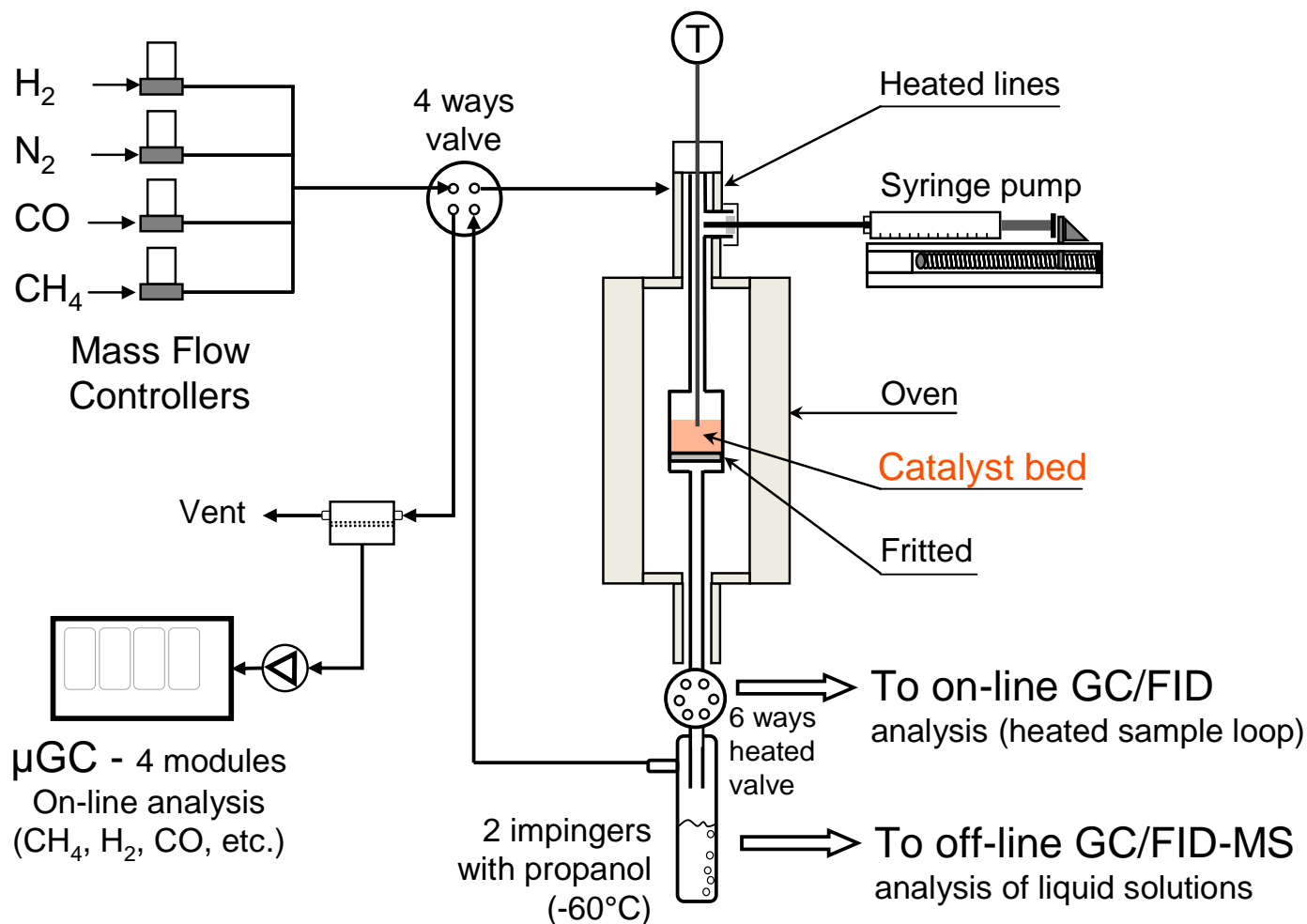
anthony.dufour@univ-lorraine.fr



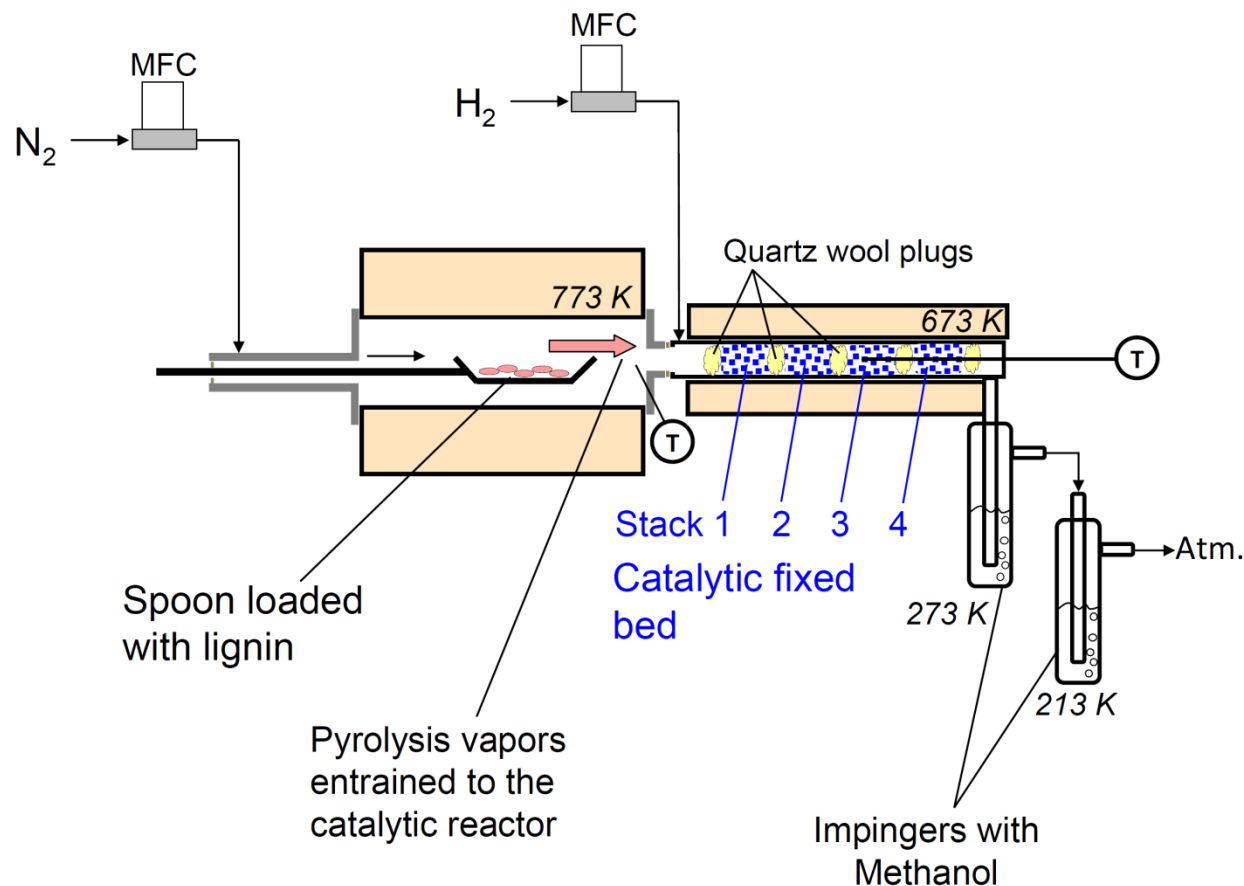
Related papers

- 1. Olcese et al., Applied Catalysis B 115-116, pp. 63-73, 2012.**
Effect of temperature, H₂ pressure and contact time on guaiacol HDO over Fe/SiO₂
- 2. Olcese et al., Applied Catalysis B 129, pp. 528-538, 2013.**
Effect of iron loads, support type (SiO₂ or carbon) and gas composition on guaiacol HDO
- 3. Olcese et al., Energy and Fuels 27 (2), pp. 975-984, 2013.**
Kinetics and Aspen Plus model of integrated lignin to BTX process
- 4. Olcese et al., Energy and Fuels 27 (4), pp. 2135-2145, 2013.**
GC*GC and petroleomic analysis on real lignin vapours HDO
- 5. Olcese et al., ChemSusChem, in press**
Mechanisms of HDO of real lignin vapours over Fe/SiO₂ and Fe/activated carbon, deactivation and coke formation

Simplified scheme of the experimental set-up for guaiacol HDO over a fixed bed of catalyst



Simplified scheme of the experimental set-up for real lignin vapours HDO



Batch lignin pyrolysis connected to an horizontal fixed bed of catalyst, with stacks to investigate the profile of coke deposit along the fixed bed length