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### Content

Effect of indigenous and external catalysts on the bio-oil production by lignocellulose fast-pyrolysis

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The effect of both indigenous (mineral components) and external (HZSM-5 zeolite) catalysts on the bio-oil production by fast-pyrolysis of different lignocellulosic biomasses has been investigated. Both woody (eucalyptus and oak) and herbaceous (miscanthus and wheat straw) materials were subjected to an acid-washing treatment that resulted effective in removing a great part of the biomass ash. Fast-pyrolysis tests of both raw and de-ashed biomasses were carried out, comparing the results obtained with and without the use of a zeolite bed for further converting the pyrolysis vapours.

De-ashing biomass significantly modified the products distribution and composition. Thus, bio-oil\* (bio-oil in water-free basis) production increased at expenses of char, water and gas fractions. The incorporation of an external HZSM-5 catalyst caused a decrease of the bio-oil\* yield due to the enhanced production of CO and gaseous olefins, as well as to the coke formation. However, in contrast with the indigenous catalysts, the HZSM-5 also induced in most cases a reduction in the bio-oil\* oxygen content. The combination of acid-washing for the removal of the mineral components with the use of the external HZSM-5 catalyst appears to be a convenient option for achieving partially deoxygenated bio-oils\* keeping their energy yield about 50% (Figure 1).

Regarding the bio-oil\* composition, both indigenous and external catalysts promotes the conversion of sugars and the formation of carboxylic acids, aldehydes and oxygenated aromatics. However, aromatic hydrocarbons were only produced over the external HZSM-5 catalyst.

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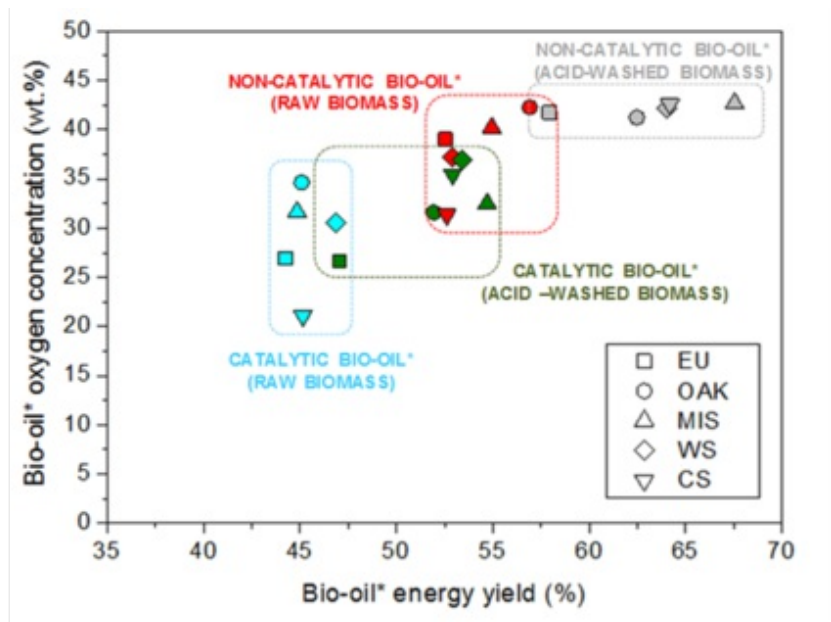


Fig. 1. Oxygen concentration versus energy yield of the bio-oil\* fraction obtained in the fast-pyrolysis tests

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**Paper title** EFFECT OF THE VINYL GROUP ON THE REACTIVITY OF LIGNIN H, G, S UNITS DURING BIOMASS FAST PYROLYSIS  
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### Content

Fast pyrolysis of lignocellulosic biomass is being considered as a viable alternative to fossil resources for the production of transportation fuels, commodity and fine chemicals. However, valorization of the lignin fraction remains a challenge despite the fact that it consists of chemically interesting aromatic functional groups. Gaining a thorough understanding of the pyrolysis chemistry of lignin would help to optimize the lignin pyrolysis process and provide guidance as to which lignin structure yields the most valuable chemicals.

Basically, lignin contains p-hydroxy phenyl (H), guaiacyl (G) and syringyl (S) units that are linked together through propanoic chains. A step forward towards the understanding of the thermal decomposition of lignin is to study the pyrolysis reactions of these three units. Most experimental data available in the literature are taken at slow heating rates and non-isothermal, multi-phase conditions. From these results it is difficult if not impossible to extract intrinsic kinetic information. Therefore, a new two-stage micro-pyrolyzer experiment with GCxGC separation and ToF-MS, FID and TCD detectors was constructed. The micro-pyrolyzer allows (a) fast pyrolysis studies of solids using only the first reactor, and (b) investigations of the gas phase chemistry of solid fuels that can be vaporized. The first stage is used for vaporization while the chemical changes take place at isothermal conditions in the plug-flow-type second reactor.

The present study describes pyrolysis results obtained with phenol, guaiacol and syringol and their para-vinyl or para-hydroxymethylvinyl substituted derivatives. Para-vinyl phenols are of interest as they are found in large quantities in bio-oils. The experimental results will be compared to predictions using literature mechanisms. The obtained chemical insights provide one essential piece of information needed for the construction of a complete lignin decomposition model.

### Acknowledgements

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**Paper-ID** 34966  
**Paper title** Efficient magnetite containing zeolite catalysts for methanol-to-hydrocarbon reaction  
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### Content

The methanol-to-hydrocarbon (MTH) reaction received considerable attention as utilizing renewable sources of both value-added chemicals and fuels becomes a priority for the society. Here, we report the development of hierarchical zeolites (ZSM-5) containing both iron oxide and nickel oxide nanoparticles. Modifying the iron oxide (magnetite, Fe<sub>3</sub>O<sub>4</sub>) amounts, we are able to control the catalyst activity and the product distribution in the MTH process. At the medium Fe<sub>3</sub>O<sub>4</sub> loading, the major fraction is composed of the C<sub>9</sub>-C<sub>11</sub> hydrocarbons (gasoline fraction). At the higher Fe<sub>3</sub>O<sub>4</sub> loading, the C<sub>1</sub>-C<sub>4</sub> hydrocarbons prevail in the reaction mixture, while at the lowest magnetite loading the major component is the C<sub>5</sub>-C<sub>8</sub> hydrocarbons. Addition of Ni species to Fe<sub>3</sub>O<sub>4</sub>-ZSM-5 leads to the formation of mixed Ni oxides (NiO/Ni<sub>2</sub>O<sub>3</sub>) positioned either on top or next to Fe<sub>3</sub>O<sub>4</sub> nanoparticles. This modification allowed us to significantly improve the catalyst stability due to diminishing coke formation and disordering of the coke formed. The incorporation of Ni oxide species also leads to a higher catalyst activity (up to 9.3 g(Methanol)/(g(ZSM-5)×h) and an improved selectivity (11.3% of the C<sub>5</sub>-C<sub>8</sub> hydrocarbons and 23.6% of the C<sub>9</sub>-C<sub>11</sub> hydrocarbons), making these zeolites highly promising for industrial applications

The research leading to these results has received funding from the European Community's Seventh Framework Programme [FP7/2007-2013] under grant agreement no. 604296.

**Paper-ID** 65791  
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## Content

Evaluating a bacterial laccase for enhancing saccharification and fermentation of steam-exploded lignocellulosic biomass

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Lignocellulosic ethanol production consists of pretreatment, enzymatic hydrolysis and fermentation steps. Pretreatment is needed to alter the lignocellulosic structure and increase the accessibility of carbohydrates to hydrolytic enzymes. Current pretreatment technologies still present several drawbacks that influence saccharification and fermentation steps. Among them, i) residual lignin can unspecifically bind hydrolytic enzymes in pretreated materials, decreasing saccharification yields; and ii) biomass-degradation products (furan derivatives, weak acids, and phenols) from pretreatment process can act as inhibitors of the hydrolytic enzymes and fermentative microorganisms. A delignification step prior to saccharification may reduce the non-productive adsorption of hydrolytic enzymes, enhancing the saccharification yields. In the same way, a detoxification process may reduce the amount of inhibitors, boosting the saccharification and fermentation steps.

Different technologies have been studied for delignification and detoxification of pretreated materials. Among them, different fungal laccases have been widely studied for improving the conversion efficiency of lignocellulose into ethanol, and consequently increasing final products concentrations. However, little is known about the use of bacterial laccases for these purposes. This study evaluates a novel bacterial laccase (MetZyme®) for enhancing the hydrolysability and fermentability of steam-exploded wheat straw. When the water insoluble solids (WIS) fraction was treated with laccase or alkali alone, a modest increase of about 5% in the sugar recovery yield (glucose and xylose) was observed in both treatments. Interestingly, the combination of alkali extraction and laccase treatment boosted enzymatic hydrolysis, increasing the glucose and xylose concentration in the hydrolysate by 21% and 30%, respectively. With regards to the fermentation stage, the whole pretreated slurry was subjected to laccase treatment, lowering the phenol content by up to 21%. This reduction allowed us to improve the fermentation performance of the thermotolerant yeast *Kluyveromyces marxianus* CECT 10875 during a simultaneous saccharification and fermentation (SSF) process. Hence, a shorter adaptation period and an increase in the cell viability—measured in terms of colony forming units (CFU/mL)—could be observed in laccase-treated slurries. These differences were even more evident when a presaccharification step was performed prior to SSF.

**Paper-ID** 42261  
**Paper title** Evaluation of diesel and biodiesel as solvents for upgrading liquefied bagasse bio-crude  
**Presentation format** Oral presentation  
**Date of submission** 30.01.2017 06:33 Uhr  
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#### **Content**

Economic upgrading of bio-crude remains one of the challenges in the development of drop-in fuels from biomass. Bio-crude was produced from thermal liquefaction of Australian sugarcane bagasse in ethanol. The whole bio-crude was extracted with both diesel and waste cooking oil biodiesel to examine the extractive potential of these solvents and the resulting bio-crude blends were then characterised. Blending ratios and temperatures were varied. Analysis of the extracts shows that polar and non-polar components in bio-crude were extracted into diesel and biodiesel, affecting physical properties such as heating value and viscosity. The potential to blend bio-crudes with conventional and renewable fuels demonstrate the viability of bio-crudes as a drop-in fuel, and the utility of extraction as an alternative to conventional refining to process bio-crude into transportation fuel.

<b>Paper-ID</b>	42786
<b>Paper title</b>	Ex-situ biomass catalytic pyrolysis to high quality bio-oil in pilot scale over novel ZSM-5 based nano-catalysts
<b>Presentation format</b>	Oral presentation
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## Content

Fast pyrolysis is a low-cost, feedstock-flexible thermochemical process that can convert low-quality lignocellulosic biomass to a liquid bio-oil fuel with high yields. Bio-oil is a complex mixture of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, and multifunctional compounds, with high water content. The high oxygen content, the presence of water and acids, and the high instability in storage render the use of bio-oil as fuel highly problematic and impose the need for extensive upgrading for its use as transportation fuel. The CASCATBEL project aims to develop a novel and feasible process for the production of high quality biofuels via the sequential coupling of three catalytic steps – pyrolysis, intermediate deoxygenation and hydrodeoxygenation, for achieving a progressive and controlled biomass deoxygenation, reducing the hydrogen consumption, and avoiding the problems that hinder other bio-oil upgrading processes.

In the frame of CASCATBEL, novel biomass pyrolysis catalysts based on hierarchical and nanocrystalline ZSM-5 promoted with weak solid oxides were developed and evaluated in lab and bench scale tests that demonstrated their promising performance. Validation of these results on pilot scale was performed in a fully automated continuous biomass pyrolysis pilot plant unit, consisting of two reactors connected in series: a fluidized bed reactor filled with inert material where thermal pyrolysis of biomass takes place and a second reactor which contains the pyrolysis catalyst for the ex-situ upgrading of the pyrolysis vapors. Tests were performed with five (5) agglomerated zeolite catalysts with different structure (normal, hierarchical and nanocrystalline) at constant temperatures (500°C for thermal pyrolysis and 450°C for the catalytic test), varying catalyst/biomass (C/B) ratio and varying time-on-stream. The increase of the C/B ratio enhanced over all materials the cracking reactions, leading to reduced bio-oil yield, with however lower oxygen content. In terms of activity, desilication of ZSM-5 led to increased cracking. Selectivity to deoxygenation is a factor equally important for catalyst evaluation. Comparison of deoxygenation selectivity at constant conversion pointed out to a nanocrystalline ZSM-5 being not only among the most active, but also the most selective catalyst, producing the highest bio-oil yield with the lowest oxygen content. Moreover, characterization of the bio-oil showed that it has the lowest acidity and the highest heating value among all catalysts. Overall, the pilot plant experiments yielded results similar to those of the bench scale tests, confirming the scalability of the catalytic materials and the process.

The work was conducted with support from the EU under the frame of the FP7 funded “CASCade deoxygenation process using tailored nanoCATalysts for the production of BiofuELs from lignocellulosic biomass – CASCATBEL” project (Grant agreement No. 604307).



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**Paper title** FCC of upgraded pyrolysis liquids mixed with crude oil distillates: strategies for improving bio-fuels quality and minimizing production costs

**Presentation format** Oral presentation

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## Content

In order to meet the EU's renewable energy targets by 2020 (up to 10% share in all forms of transportation fuels<sup>1</sup>), a realistic alternative to first generation bio-fuels is to produce hybrid bio/fossil fuels by co-refining biomass pyrolysis liquids (PL) with crude oil fractions in a conventional oil refinery<sup>2</sup>. However, co-refining may lead to severe changes in products quality, such as a higher aromaticity and residual oxygenates in the hybrid fuels that are produced. For the case of co-FCC (fluid catalytic cracking), various strategies can be implemented to limit those impacts along this complex value chain ranging from bio-mass to bio-gasoline.

A first strategy is to preserve the gasoline yield and quality by implementing a PL hydrotreating prior to co-processing, to lower their oxygen content<sup>3</sup>. However, to reduce the cost impact of hydrogen consumption for severe hydrotreating levels, a balance in PL upgrading severity/efficiency has to be found<sup>4</sup>. This presentation analyzes the changes in conversion, yields and gasoline composition (aromatics/olefins vs saturated alkanes) as a function of the bio-oils hydrotreating severity, measured in a Micro Activity Test (MAT) reactor. It is shown that a compromise can be reached between bio-oil upgrading severity and FCC products yields and quality (RON, PIONA analysis).

A second strategy is to adapt the FCC catalysts to the presence of oxygenate molecules typical of the bio-feedstock still present in the upgraded pyrolytic liquids. Y zeolites, main active component in FCC catalysts, are up-graded by creating a mesoporosity in addition to the microporosity to favor the diffusion of the large lignocellulosic fragments throughout the cracking catalysts, according hierarchical post synthesis processes<sup>5,6</sup>. It is shown that significant changes in the gasoline composition (aromaticity, olefinicity) can be achieved by these processes, based on major changes in porosity and intrinsic diffusivity of feed molecules.

The never reported combined impact for these two strategies on the co-FCC efficiency is discussed as a potential guideline for minimizing the cost of bio-oils upgrading and thereof the hybrid transportation fuels, while maintaining their quality.

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1 [http://ec.europa.eu/energy/renewables/targets\\_eu.htm](http://ec.europa.eu/energy/renewables/targets_eu.htm)

2 Schuurman, Y.; Fogassy, G.; Mirodatos, C.; in "The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals", Eds Triantafyllidis, Stöcker and Lappas, Elsevier, 2013, 321–349

3 Elliott, D. C. *Energy Fuels* 21 (2007) 1792-815

4 Gueudre, L.; Chapon, F.; Mirodatos, C.; Schuurman, Y.; Venderbosch, R.E.; Jordan, E; Wellach, S.; Gutierrez-Miravalles, R.; *Fuel* 192 (2017) 60-70

5 Garcia-Martinez, J.; Johnson, M.; Valla, J.; Li, K.; Y. Ying, J.; *Catal. Sci. Technol.* 2 (2012) 987–994.

6 Chal, R.; Cacciaguerra, T.; van Donk, S.; Gerardin, C., *Chem. Com.* 46 (2010) 7840-7842.