

# One-pot synthesis of liquid fuel by conversion of lignocellulosic biomass over Ni/H- $\beta$ zeolite

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## Introduction

Growing concerns about global climate change and the volatility of fossil fuel markets have resulted in an ever-increasing shift of global energy policies to seek the sustainable manufacturing of *drop-in* hydrocarbon fuels from renewable sources, such as lignocellulose.<sup>1</sup> Many biomass-to-liquid fuel strategies are being actively developed, including thermochemical processes and depolymerization of biomass into intermediates followed by their hydrodeoxygenation (HDO).<sup>2</sup> These technologies have been implemented with limited success because they are often energy-intensive, require multi-step approaches, and are characterized by relatively low total carbon recoveries.<sup>3</sup> This situation suggests that the development of a direct route from lignocellulose to alkanes and aromatics could be highly desirable from an economical and process design point of view, especially if it could be integrated within existing petroleum refineries.

In the present study, we developed a one-pot process for the hydrodeoxygenation (HDO) of poplar into alkanes (C<sub>3</sub>-C<sub>10</sub>) and aromatics by using Ni/H- $\beta$  zeolite catalyst. This process focuses on maximizing the balance between cleavage and coupling pathways to allow the access to chemical diversity in products, which is necessary to achieve the production of *drop-in* fuels.

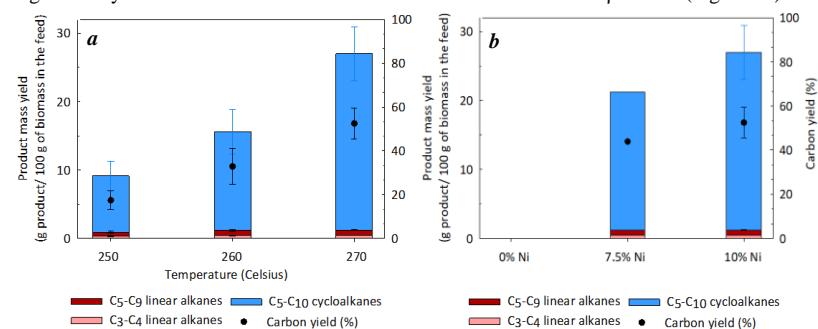
## Materials and Methods

H- $\beta$  zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> =25) was prepared by the hydrothermal method reported elsewhere.<sup>4</sup> Ni/H- $\beta$  zeolites with different Ni contents were prepared by the incipient wetness impregnation method. The total acidity and the nature of acid sites (Lewis and Brønsted) within the catalysts were determined by NH<sub>3</sub>-TPD (Temperature programmed desorption) and pyridine-FTIR (Transmission Fourier transform infrared spectroscopy). Experimental runs were carried out in a 100 mL Parr batch reactor at 1:0.5 poplar to catalyst ratio (w/w) using cyclohexane solvent, 3 MPa of initial H<sub>2</sub> pressure, and reaction temperatures ranging from 250 to 300 °C for 6 h of reaction time. The experimental analysis involved the identification and quantification of the liquid products using GC-MS (Gas chromatography-mass spectrometry).

## Results and Discussion

Here, we report the catalytic conversion of poplar carbohydrates into a wide range of linear and cycloalkanes (C<sub>3</sub>-C<sub>10</sub>) with a 25.8±3.6% mass yield in the presence of Ni/H- $\beta$  zeolite, and at relatively mild conditions (Figure 1a). Minor formation of oxygenated (<2 wt%) and

aromatic compounds (5 wt%) was found at 270 °C, which indicates that Ni/H- $\beta$  zeolite is highly selective toward HDO reactions of carbohydrates. In addition, the effect of varying metal loading (0%, 7.5%, and 10%) on the conversion of biomass carbohydrates into liquid alkanes was also evaluated. In the absence of Ni loading, even though a biomass conversion of 59% was observed, no liquid alkanes were produced. The addition of Ni loading on H- $\beta$  zeolite significantly enhanced the formation of alkanes relative to 0% Ni/H- $\beta$  zeolite (Figure 1b).



**Figure 1.** Effect of temperature (a) and effect of metal loading (b) on the mass yield of alkanes and total carbon recovery. Reaction conditions: a - 10% Ni/H- $\beta$  zeolite (0.5 g), poplar (1 g), H<sub>2</sub> (3 MPa) and 6 h; b -catalyst (0.5 g) poplar (1 g), T (270 °C), H<sub>2</sub> (3 MPa) and 6 h.

In addition, increasing reaction temperature from 270 to 300 °C was found to be crucial to promote the cleavage of lignin  $\beta$ -O-4 bonds and further HDO reactions, resulting into a final aromatic yield of 24.6% (results not shown).

## Significance

Here, we show that i) carbohydrates are selectively converted to liquid hydrocarbons, predominantly cycloalkanes, at lower temperatures than lignin, ii) our catalytic system can perform HDO of carbohydrates while preserving aromatic moieties in the system; and iii) this process is capable of some level of oligomerization to high-carbon alkanes from carbohydrates.

## References

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