

SUPERCRITICAL DEOXYGENATION OF PYROLYSIS BIO-OIL COMPOUNDS

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Summary

A novel process for the fixed-bed deoxygenation of oxygenated biomass compounds in supercritical media at mild pressures (tens of bars) is presented. As an example, nonanal deoxygenation over Pt/Al₂O₃ in supercritical *n*-hexane ($T_c = 234.45^\circ\text{C}$, $P_c = 30.2$ bar) with excess hydrogen at 300°C and 45 bar provides conversions as high as 80% with over 75% selectivity to C₈ and C₉ hydrocarbons, at liquid hourly space velocities up to 200 g substrate/(g Pt * hr). The enhanced rates are attributed to the complete miscibility of the substrate and hydrogen in supercritical hexane, eliminating the gas-liquid mass transfer resistances present in conventional systems.

Keywords

Process intensification, biomass processing technologies, Green CRE

Introduction

Bio-oils derived from biomass pyrolysis show much promise as feedstocks for producing hydrocarbons that may be readily integrated as feeds into existing petroleum refineries as well as future biorefineries. Current utilization of these bio-oils is limited by their poor stability, attributed primarily to their high oxygen content.¹ Numerous upgrading strategies that improve bio-oil quality and/or reduce oxygen content are presented in the literature, including hydrogenation and hydrodeoxygenation,²⁻⁴ esterification,^{5, 6} and selective extraction.^{7, 8} A key limitation for many of the proposed bio-oil upgrading schemes is the requirement for high hydrogen partial pressures (up to ~300 bar) to enhance the intrinsic H₂ solubility in the liquid phase.

Catalytic deoxygenation of bio-oil in supercritical solvents can potentially eliminate the H₂ solubility limitation by bringing the reactants and hydrogen into a single phase. Supercritical hydrogenations have many advantages as described in a recent review by Baiker et al. and the references therein.⁹ In addition to eliminating interphase mass transfer resistances, the enhanced extraction of heavy hydrocarbons from the catalyst pores by the near-critical reaction mixture alleviates internal pore-diffusion limitations.¹⁰ This paper presents the first results of supercritical deoxygenation – by simultaneous hydrogenation, decarbonylation, or decarboxylation – of some model oxygenates.

Experimental

The reactions were performed in a continuous fixed-bed reactor at 300°C over supported noble-metal catalysts. Specifically, the deoxygenation of nonanal, nonanoic acid,

and related compounds is presented using supercritical *n*-hexane ($P_c = 30.2$ bar, $T_c = 234.45^\circ\text{C}$) as the solvent. The reactor effluent was sampled and analyzed by GC online to quantify both liquid phase and gas phase products. The temperature was measured with a profile thermoprobe and the reactor pressure was controlled with a back-pressure regulator.

Results

Our initial results show outstanding potential for the supercritical deoxygenation concept. As shown in Figure 1, the deoxygenation of nonanal proceeds via both hydrogenation (to nonanol and nonane) and decarbonylation (to octane) pathways. Substrate conversions of 70-80% are obtained.

In Figure 2, the reactor productivity reaches a maximum of over 200 g substrate/(g Pt * hr) at 1.5-2.0 $P_{c,\text{hexane}}$ (45-60 bar). Selectivity to hydrocarbons approaches 80% at these conditions. This indicates that the reaction becomes pore-diffusion limited at higher supercritical pressures due to decreasing diffusivity of the liquid-like reaction mixtures.¹¹ The fact that the milder near-critical pressures are optimal has also been observed previously during Fischer-Tröpsch synthesis in supercritical hexane¹² and favors process economics. Extended runs (Figure 3) showed that the conversion and selectivities are stable throughout the 16 h duration.

These promising results along with the deoxygenation of other model oxygenated species, including carboxylic acids, alcohols, and phenolic compounds, will be presented along with full characterization of liquid/gas

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phase products as well as the BET surface area/pore volume of fresh and spent catalysts. Mathematical modeling of the fixed-bed reactor data will be presented to explain the beneficial effect of pressure-tuning on the deoxygenation rates and selectivities.

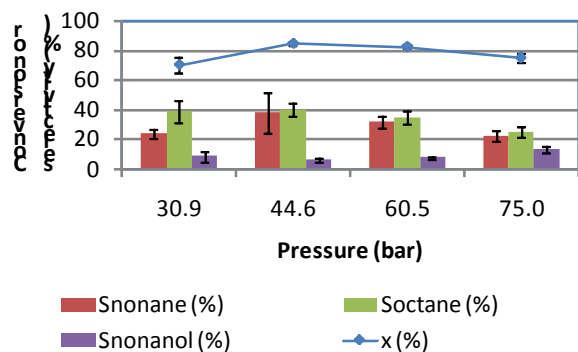


Figure 1. Conversion and selectivity for nonanal deoxygenation. Reaction conditions: $m_{\text{Pt}/\text{Al}_2\text{O}_3} = 2$ g, $T = 300^\circ\text{C}$, $F_{\text{C}_9} = 0.0003$ mol/min, $F_{\text{H}_2} = 0.009$ mol/min.

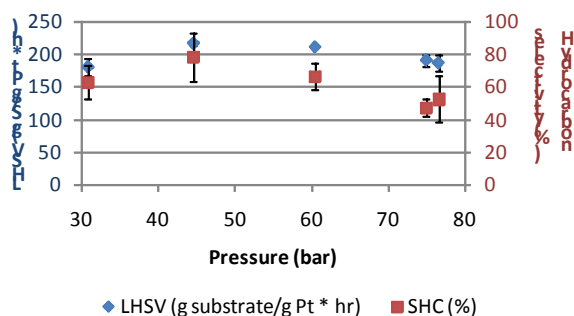


Figure 2. Liquid hourly space velocity and hydrocarbon selectivity for nonanal deoxygenation. Reaction conditions: $m_{\text{Pt}/\text{Al}_2\text{O}_3} = 2$ g, $T = 300^\circ\text{C}$, $F_{\text{C}_9} = 0.0003$ mol/min, $F_{\text{H}_2} = 0.009$ mol/min.

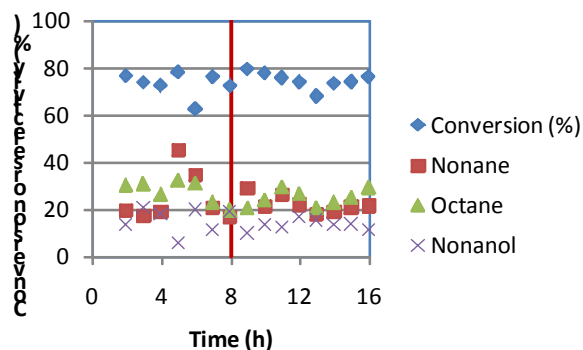


Figure 3. Conversion and selectivity for reactions on consecutive days with same catalyst and reaction conditions: $m_{\text{Pt}/\text{Al}_2\text{O}_3} = 2.009$ g, $T = 300^\circ\text{C}$, $P = 75$ bar, $F_{\text{C}_9} = 0.0003$ mol/min, $F_{\text{H}_2} = 0.009$ mol/min.

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