



Wood-derived olefins by steam cracking of hydrodeoxygenated tall oils

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HIGHLIGHTS

- ▶ Tall oil fatty acid and distilled tall oil hydrodeoxygenation produces paraffinic liquids.
- ▶ Steam cracking of hydrodeoxygenated tall oils at pilot plant scale.
- ▶ High light olefin yields when cracking hydrodeoxygenated tall oil fatty acids.
- ▶ Pilot plant cokes test indicates that reasonable run lengths can be expected.

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ABSTRACT

Tall oil fractions obtained from Norwegian spruce pulping were hydrodeoxygenated (HDO) at pilot scale using a commercial NiMo hydrotreating catalyst. Comprehensive two dimensional gas chromatography (GC × GC) showed that HDO of both tall oil fatty acids (TOFA) and distilled tall oil (DTO) produced highly paraffinic hydrocarbon liquids. The hydrotreated fractions also contained fatty acid methyl esters and norabietane and norabietatriene isomers. Steam cracking of HDO–TOFA in a pilot plant revealed that high light olefin yields can be obtained, with 35.4 wt.% of ethene and 18.2 wt.% of propene at a coil outlet pressure (COP) of 1.7 bara, a dilution of 0.45 kg_{steam}/kg_{HDO–TOFA} and a coil outlet temperature (COT) of 820 °C. A pilot plant coking experiment indicated that cracking of HDO–TOFA at a COT of 850 °C results in limited fouling in the reactor. Co-cracking of HDO tall oil fractions with a typical fossil-based naphtha showed improved selectivity to desired light olefins, further demonstrating the potential of large scale olefin production from hydrotreated tall oil fractions in conventional crackers.

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1. Introduction

Ethene, propene, 1,3-butadiene, benzene, toluene and xylenes are produced and consumed in enormous amounts every year, as these base chemicals are the building blocks for most polymers and the starting materials for many additives, solvents, and other high-value chemicals. Currently, steam cracking of fossil feedstocks is mainly responsible for their production. For example 140 × 10⁶ tons of ethene were produced in 2010 with an estimated growth rate of 5.3% (Zimmermann and Walzl, 2009). Therefore, producing these chemicals from renewable resources represents an enormous opportunity, and would contribute to the transition from a petrochemical to a green chemical industry.

Recent research has focused on several alternative technologies for production of olefins such as bio-ethanol dehydration (Kagyrmanova et al., 2011), methanol-to-olefins (MTO) (Chen

et al., 2005), catalytic fast pyrolysis of lignocellulosic biomass (Carlson et al., 2011; Lavoie et al., 2011), bio-oil upgrading (Gong et al., 2011), etc. However, despite these research efforts and despite continuously increasing oil prices, petroleum conversion and petrochemical production processes are still highly profitable and crude oil remains the most important resource used by the chemical industry. The main reasons are the magnitude of past investments and the operating scale of current units. The use of biomass-derived feedstocks in existing conversion and production units is therefore a very interesting option, since it would allow production of renewable fuels and chemicals without the need to build new production facilities (Huber and Corma, 2007). For example, fluid catalytic cracking (FCC) of vegetable oils, or their mixtures with vacuum gas oil, using conventional FCC technology has already been studied (Bielansky et al., 2011; Dupain et al., 2007; Melero et al., 2010). However, although process conditions can be optimized to maximize propene yields, FCC is mainly used to produce liquid fuels. Alternatively, several types of low cost biomass resources are, after effective upgrading, suitable renewable

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