

Lignin conversion to partially oxygenated biogasolines and alkoxyaromatic gasoline blending components

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A two-stage process for high-yield lignin conversion to partially oxygenated biogasoline has been recently developed.[1] Stage I of the process involves mild base-catalyzed depolymerization (BCD) of lignin, followed by non-deoxygenative hydrotreatment (HT) to yield an intermediate product consisting mainly of monocyclic phenols. In Stage II, this intermediate phenolic product is subjected to etherification (ETR) with methanol to yield a partially oxygenated biogasoline, consisting of a mixture of (substituted) phenyl methyl ethers and cycloalkyl methyl ethers, C₇-C₁₀ alkylbenzenes, C₅-C₁₀ (mostly multibranched) paraffins, and polyalkylated cycloalkanes.[1,2] Some basic features of the process are summarized in Figure 1. Low-temperature (240-270 °C) BCD in Stage I proceeds with preservation of most of the lignin oxygen. In the supplemental mild hydrotreatment (HT), in the presence of the indicated Pt-modified solid superacid catalysts, the lignin depolymerization is completed by selective C-C hydrocracking of some oligomeric phenols (present in the BCD product) with a low extent of competing C-O hydrogenolysis. The resulting, fully depolymerized lignin is subjected in Stage II to superacid-catalyzed etherification (ETR) with methanol to yield the final, partially oxygenated biogasoline product. [1,2]

The BCD-ETR process (Figure 1) can be adapted for preferential production (selectivity, 75 - 85 wt%) of methoxybenzenes having 0 to 2, predominantly 1 or 2, ring substituents. This can be achieved by essentially eliminating any ring hydrogenation and controlling the extent of hydrodealkylation of intermediate phenols during the HT step (Stage I). The final C₇-C₉ methoxybenzene products have critically important advantages as high octane additives in comparison with other O-containing compounds, in particular dialkylethers, e.g., methyl-*t*-butyl ether (MTBE). The latter has been recently rejected as a gasoline additive, due to (a) its high volatility (b.p., 55 °C) and the associated unacceptable level of air polluting effect, and (b) its high solubility in water and consequent undesirable pollution effect on underground water. In contrast, C₇-C₉ methoxybenzenes are characterized by relatively lower volatility (b.p.'s in the range of 154 - 195 °C) and consequent lack of any significant effect on air pollution, as well as lack of solubility in water and anticipated lack of any pollution effects on underground water. A second major advantage of C₇-C₉ methoxybenzenes is their extraordinarily high blending octane numbers in the approximate range of 142 - 166. These superior properties, coupled with the anticipated high efficiency of the low temperature BCD-ETR procedure, indicate that lignin-derived C₇-C₉ methoxybenzenes could provide an ideal replacement of currently discredited dialkylethers as choice octane enhancers for petroleum-derived hydrocarbon gasolines.

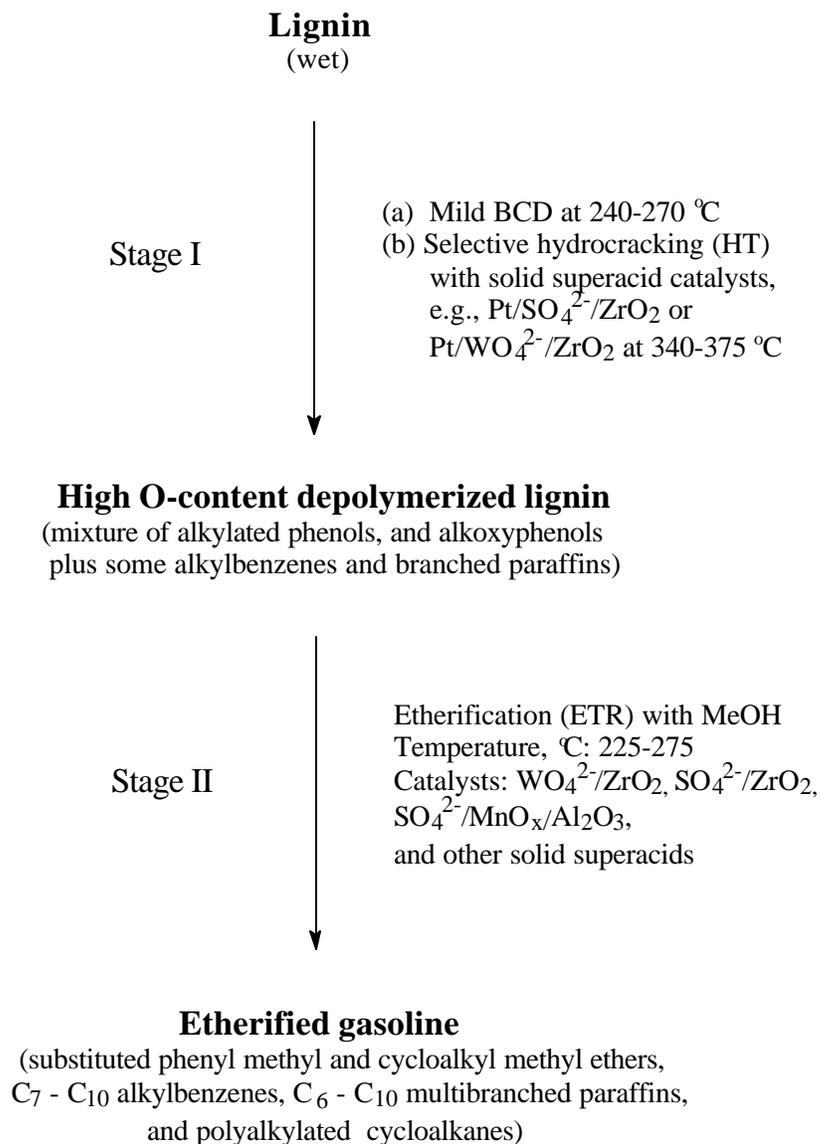


Figure 1. Scheme of two-stage (BCD-ETR) process for lignin conversion to reformulated, partially oxygenated biogasoline.

References:

1. Shabtai JS, Zmierczak WW, Chornet E. U.S. Patent, 6, 172, 272 (Jan. 2001).
2. Kadangode S. *Ph. D. Dissertation*, University of Utah, 2001.