

Catalytic oxidative depolymerization of organosolv lignins

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Introduction

Lignin is a abundant, yet recalcitrant raw material stream available from biorefineries. Although used in some specialty applications, most lignin is currently used in low value energy generation in paper mills. Potential uses are numerous, but all hinge on the availability of technology to efficiently convert lignin into monomers or other bulk chemicals. The molecular weight distribution of the product of the depolymerization process is a important indicator of the efficacy of the conversion process and the applicability of the reaction products.

Lignin varies in chemical structure depending on the biomass source and fractionation method. We have compared a ethanol and a acetic acid/formic acid organosolv lignin. Organosolv lignin is obtained by extracting lignocellulosic biomass with a mixture of a organic solvent and water.

Experimental

All experiments were performed in a fed batch 500 mL Hastalloy C Büchi autoclave. Reaction pressure was kept at 30 bar, reaction times were varied between 1 and 4 hours and the temperatures between 150 and 220 °C. The oxidant was compressed air. In each reaction, 10% lignin by weight was used. Ethanol and acetic acid/formic acid organosolv lignins were used as received. Monomeric compounds were analyzed by GC-MS whereas the oligomeric fractions and the lignins were characterized by HP-SEC using 0.5 M NaOH[2].

Results/Discussion

The ethanol organosolv lignins were oxidized in a mixture of formic (10%) and acetic acid. This lignin is very soluble in formic acid and adding a small amount of formic acid to acetic acid allowed for total dissolution of the lignin. During the reaction a solid product precipitates from the solution. ATR analysis of the samples yielded little useful information. Representative samples of the solids were analyzed by HPSEC. The results are listed in Table 1. The molar mass seems to increase during the reaction which would suggest that the lignin recondenses at reaction conditions.

Table 1: Results of the HPSEC analysis of the oxidation products of ethanol organosolv lignin.

T, °C	Air (SCCM)	*Co (mM)	*Mn (mM)	M _w [†]	M _n [†]	M _z [†]	PDI [†]
180	400	0	0	10820	1549	65929	6.99
220	800	0	0	8334	1781	26331	4.68
180	400	5	5	8724	1389	43344	6.28
Ethanol organosolv lignin				7080	1352	28120	5.24

[†]M_w = average molecular weight, M_n = number average, M_z = z-average, PDI = poly-dispersity index.

The acetic acid organosolv lignin does not dissolve appreciably in formic acid. Thus all experiments were conducted in glacial acetic acid. No significant amounts of monomeric phenols were detected in the reaction mixture. Only at low temperatures did we observe small amounts of monomeric phenols. The solids from the reaction were analyzed by HP SEC. The molecular weight decreases with increasing catalyst concentration, increasing reaction temperature and increasing reaction time (Table 2). This results contrast the pure batch experiments performed at much higher pressures[1]. The results demonstrate the efficacy of this oxidation process.

Table 2: Results of the characterization product of oxidation of acetic acid/formic acid lignin.

Temp (°C)	Time (min.)	*Co, mM	*Mn, mM	*Br ⁻ , mM	*Zr, mM	M _w [†]	M _n [†]	M _z [†]	PDI [†]
Acetic acid formic acid lignin						40,733	7,028	124,202	5.80
220	120	0	0	0	0	11,991	4,356	31,599	2.75
220	120	15	15	15	0	8,888	3,671	20,715	2.42
220	240	15	15	15	0	7,951	3,217	19,784	2.47
180	120	15	15	15	0	14,212	4,407	36,389	3.22
150	120	15	15	15	0	13,528	4,369	34,058	3.10
180**	120	6.9	6.9	13.8	6.9	16,330	5,471	39,563	2.98
220	240	5	15	15	0	8,476	3,583	20,066	2.37
220	240	15	5	15	0	9,090	3,798	22,953	2.39
220	240	5	5	5	0	8,534	3,586	20,735	2.38

*Catalysts are Co(OAc)₂, Mn(OAc)₂, Zr(OAc)₂, and 1-Butyl-3-methyl imidazolium bromide.

** 8% lignin.

References.

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