Catalytic reductive fractionation (CRF): effects of acidic/alkaline additives

Tom Renders,* Sander Van den Bosch,* Steven-Friso Koelewijn,* Thijs Vangeel,* Gil van den Bossche,* Wouter Schutyser,†,‡ Bert Sels*†

* Center for Surface Chemistry and Catalysis, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium
† National Bioenergy Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, Colorado 80401, United States
‡ E-mail: wouter.schutyser@biw.kuleuven.be, bert.sels@biw.kuleuven.be

Classic cascade
Focus on valorization of carbohydrates, not on lignin
Degradation & repolymerization: technical lignins
Recalcitrant substrate, low monomer yields
Low added-value, lignin incineration

Lignin-first cascade
Focus on valorization of native lignin, prior to sugars
Prevention of degradation & repolymerization
Reactive substrate, high monomer yields
Increased added value from lignin

The CRF-biorefinery

Process summary: Turning the lignin-first paradigm into reality is enabled by a process termed catalytic reductive fractionation (CRF). Herein, lignin is solvolytically extracted from the biomass matrix (step 1), followed by instant catalytic depolymerization (hydrogenolysis, step 2). The main products resulting from this biorefinery are a depolymerized lignin oil and a carbohydrate enriched pulp.

Pitfall: High temperatures (523 K) are required in order to obtain a near complete delignification, which implies a high operating pressure (120 bar).

Possible solution: Catalytic additives (H₃PO₄, NaOH) could possibly assist the solvolytic lignin extraction (step 1) at milder T (473 K) and P (60 bar).

Research question: What are the effects of acidic (H₃PO₄) or alkaline (NaOH) additives on the CRF process? Are these effects beneficial?

Effects on lignin

Lignin
- Increased monomer yield
- Increased delignification
- Higher lignin conversion at milder T
- Similar outcome as high T reference

Pulp
- Removal of hemicellulose (alcoholysis)
- Effective preservation of cellulose
- Cleaner cellulose pulp

Evaluation

Effects on pulp

Lignin
- Decreased monomer yield
- Increased delignification
- Lower monomer selectivity (cfr. gap)
- Hampered depolymerization by NaOH

Pulp
- Partial loss of hemicellulose
- Partial loss of cellulose
- Degradation of released sugars