

Optimised use of hydrogen peroxide during the delignification step in an organosolv biorefinery process

① Background: use of peracids as delignifying agents

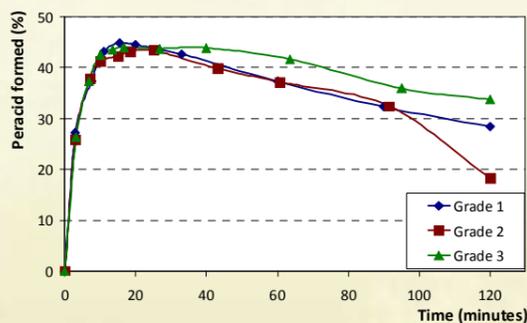
The initial step of the organosolv biorefinery process considered in the Biocore project is based on the use of acids and peracids to produce three separate streams of: cellulose, C5 sugars and lignin. The results presented on this poster are focused on the delignification stage that involve the use of peracids.

Preliminary experiments were conducted to characterize the generation of peracids in the reference process conditions: addition 1.8 % of H₂O₂ in an acid solution containing 55 % acetic acid, 30 % formic acid and 15 % water.

Method: Accurate determination of the respective H₂O₂ and peracid concentration was based on the successive titration of H₂O₂ with potassium permanganate and of peracids with sodium thiosulfate.

Results: Peracid formation is expressed (in %) as the molar ratio of peracid formed to the amount of hydrogen peroxide involved

Fig. 1: Peracid formation over time (fixed H₂O₂ charge, different grades)



The quantity of peracids formed is peaking after about 20 minutes and then slowly decreasing with time. Differences according to H₂O₂ grades were observed regarding the level of generated peracids. With Grade 3, more than 40% conversion of H₂O₂ into peracids could be maintained during 1 hour

② Improvement of peracid generation with H₂O₂

Considering the kinetics of delignification that show a fast reaction during the first 10 minutes and then a slower reduction of the lignin content, studies were conducted in order to optimise the biomass delignification with peracids.

• Delignification trials

Peracid formation is promoted by high H₂O₂ concentration so the idea was to maintain a sufficiently high H₂O₂ concentration during the delignification stage that lasts 90 minutes. A practical solution that was identified consisted in splitting the H₂O₂ addition during the course of the delignification stage.

Fig. 2: Various ways to add H₂O₂ and resulting delignification level after 90 min.

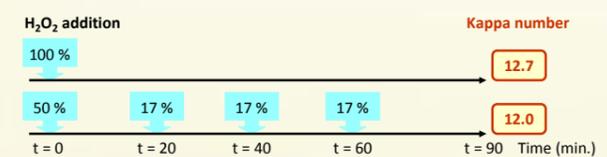
Process conditions for the delignification stage with biomass (wheat straw):

Temperature: 80 °C

Retention time: 90 minutes.

Pulp concentration: 12.5% weight in (55% acetic acid + 30% formic acid + 15% water) corresponding to 12.5% dry solid + 87.5% liquid

Total H₂O₂ charge: 100 kg/t_{dry pulp}



• Monitoring of peracids formation

A study was conducted to measure H₂O₂ and peracids concentration in the filtrates along the delignification stage.

Methodology

A titration method based on successive titration of peracids and H₂O₂ with sodium thiosulfate at 0 °C was applied on the filtrates sampled out of the pulp during the delignification stage just after (23') or before (39', 59') H₂O₂ additions.

Sampling time	23 min.	39 min.	59 min.
H ₂ O ₂ addition	120 kg at t=0		
[Per] in mmol/L	14	0	0
[H ₂ O ₂] in mmol/L	13	0	0
H ₂ O ₂ addition	60 kg at t=0 + 20kg at t=20', t=40' & t=60'		
[Per] in mmol/L	27	0.9	1.2
[H ₂ O ₂] in mmol/L	55	0.7	1.2

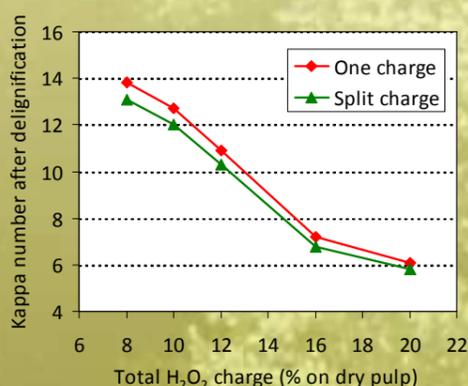
In the case of staged addition of H₂O₂, higher concentrations of peracids and H₂O₂ are measured during delignification. This could explain why better delignification efficiency (lower kappa number) is observed when staged addition of H₂O₂ is implemented.

③ Base case: Delignification of wheat straw

The interesting strategy developed in ② was implemented on wheat straw over a wider range of conditions. The key parameter used to follow the delignification stage is the kappa number of the pulp and it is measured according to the standard method ISO 302.

Material: pulp from CIMV pilot sampled after extraction stage. Initial kappa number 28. Process conditions as for Fig. 2.

Fig. 3: Delignification of wheat straw with variable H₂O₂ charges and for each total H₂O₂ charge, addition was done all at t = 0 ("one charge") or split in several fractions over the 90 minutes as described in ② (1/2 and then 3 times 1/6 called "split charge").



Whatever the total H₂O₂ charge, staged additions (1/2 and then 3 times 1/6 of total charge) allow to achieve a kappa number 5% lower than a single addition corresponding to a reduction by 5 to 10% of H₂O₂ required charge. There is a technical and economical interest in splitting the H₂O₂ charge

④ Delignification of hardwood feedstock (poplar)

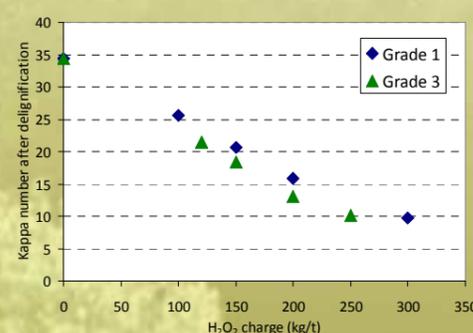
In order to evaluate the versatility of this organosolv biorefinery process, delignification trials were conducted with hardwood (poplar, supplied by CAPAX) as a raw material. The extraction conditions had to be modified (higher formic acid ratio) to allow satisfactory processing.

Process conditions with poplar:

Temperature: 80°C - Retention time: 90 minutes.

Solvent blend: 30% acetic acid + 55% formic acid + 15% water

Fig. 4: Delignification of poplar with variable H₂O₂ charges (single addition)



Final kappa numbers are higher than with straw. Higher H₂O₂ charge is required to achieve same delignification degree. Main effect due to H₂O₂ formulation: Kappa number is 10 % to 15 % lower corresponding to a reduction by 10 to 20 % of H₂O₂ required charge

⑤ Conclusions

The work conducted on the delignification stage of the organosolv biorefinery process lead to significant progress in the understanding and optimisation of this step.

Regarding the use of hydrogen peroxide (H₂O₂), a specific arrangement of its addition to the acid blend (a larger first fraction representing half the total followed by 3 equivalent fractions) significantly improved the delignification of straw allowing a reduction by 5 to 10% of H₂O₂ required charge.

In addition, specific H₂O₂ grades were developed to further improve the performance and they proved to be of particular interest in the case of hardwood feedstock. A patent application has been filed.