Organosolv fractionation of lignocellulosic biomass for an integrated biorefinery

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FOR AN INTEGRATED BIOREFINERY

The economics of lignocellulosic biorefineries would substantially improve with value-added applications for lignin. Organosolv fractionation processes for lignocellulosic biomass can be a way towards this end. Two organosolv fractionation processes were compared as part of the EU FP7 BIOCORE project: the CIMV acetic acid / formic acid process and the ethanol organosolv process. It was found that both processes have a clear potential within the field of biorefining. The CIMV process seems more suitable to produce sugars from the hemicellulose fraction, whereas the ethanol organosolv process yields lignin with a higher purity.

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INTRODUCTION BIOREFINERY

Globally, a limited number of biorefineries that use lignocellulosic biomass as feedstock are currently in operation or under construction (**Table 1**). Most lignocellulosic biorefineries primarily aim at utilization of sustainable carbohydrates from (hemi)cellulose. However, there currently exist few commercial applications for lignin other than combustion. Value-added applications for lignin would substantially improve the economics of a lignocellulosic biorefinery. A recent article in this journal gave a general introduction on lignin **[3]**. In an earlier paper on organosolv in NPT Procestechnologie, the applications of lignin were discussed and it was stated that sulphur-free lignins are preferred, in particular organosolv lignins **[4]**. Because of its relatively higher homogeneity, purity, and reactivity, organosolv lignins are promising and probably 'first choice' candidates for direct applications as well as for further processing **[1]**.

TABLE 1: EXAMPLES OF LIGNOCELLULOSIC BIOREFINERIES

COMPANY	FEEDSTOCK	FRACTIONATION PROCESS	SCALE	MAIN PRODUCT	LIGNIN USE
BETA RENEWABLES (Italy)	agricultural residues	steam explosion	commercial	bioethanol	fuel
ABNT (USA)	corn stover, wheat straw, switch grass	steam explosion	commercial	bioethanol	fuel for steam and electricity
POET - DSM (USA)	agricultural residues	enzymatic hydrolysis	commercial	bioethanol, biogas	fuel
ABNT (Spain)	wheat straw	steam explosion	demo	bioethanol	fuel, feed additive
CHEMPOLIS (Oulu, Finland)	agricultural residues	organosolv	demo	cellulose, bioethanol	fuel
INBICON (Denmark)	agricultural residues	hydrothermal	demo	bioethanol	fuel
CIMV (France)	agricultural residues (e.g. wheat and rice straw), hardwoods	organic acid and organosolv	pilot	cellulose, C5 sugars, lignin	performance materials
SEKAB/EPAB (Sweden)	wood chips, bagasse, wheat straw, energy grass, corn stover	one step dilute acid enzymatic pretreatment	pilot	bioethanol	fuel and performance materials
CLARIANT (Germany)	wheat straw	pressurized steam treatment and enzymatic hydrolysis	pilot	bioethanol	fuel

ORGANOSOLV FRACTIONATION

Organosolv is based on the treatment of biomass with an (aqueous) organic solvent at elevated temperatures **[5-8]**. Commonly used solvents are ethanol, methanol, acetone and organic acids like acetic acid and formic acid or combinations thereof. Organosolv processes delignify lignocellulose, with the organic solvent functioning as lignin extractant, while the hemicellulose is depolymerized through acid-catalysed hydrolysis. In general, organosolv processes aim to fractionate the lignocellulosic biomass as much as possible into its individual major fractions in contrast to other pre-treatment technologies such as steam explosion and dilute acid hydrolysis. These technologies merely make the cellulose fraction suitable for further processing without recovery of a purified lignin fraction.

Organosolv lignin has a high purity (limited amounts of residual carbohydrates and minerals) due to its isolation process. Consequently, its application spectrum is broader compared to the more impure lignin-containing residues derived from conventional pre-treatments which are targeted primarily towards the production of cellulose for paper or second generation bioethanol. The latter are a complex mixture of unconverted carbohydrates, lignin, minerals and process chemicals or microbial residues. Hardly any applications for such complex by-products have been identified other than combustion for combined heat and power (CHP). Organosolv lignins also have a relatively low molecular weight with a narrow distribution and a very low sulphur content.

TABLE 2: QUALITATIVE COMPARISON BENCHMARKING CIMV VS ECN PROCESSES (ADAPTED FROM [11])

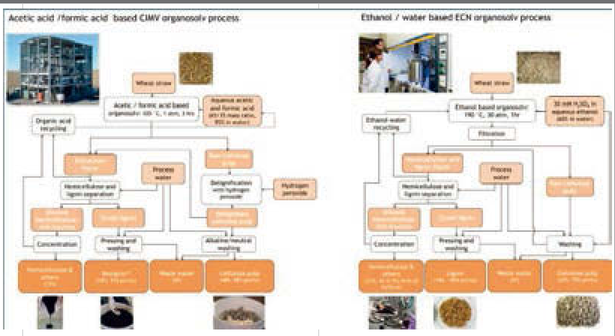

Fig 1

		ACETIC FORMIC ACID BASED CIMV	ETHANOL BASED ECN ORGANOSOLV
POSSIBLE FEEDSTOCKS		straws, agricultural residues, hardwoods	straws, agricultural residues, hardwoods, spruce
SCALE OF DEVELOPMENT		40 kg/h (continuous)	1,5 kg in 20 l batch reactor (autoclave
ENZYMATIC DIGESTIBILITY AND FERMENTABILITY	cellulose pulp	very good enzymatic hydrolysis and fermentation to e.g. ethanol	good enzymatic hydrolysis and fermentation to ethanol
	hemicellulose-rich fraction	can be fermented after purification	partly degraded to furfural. Purification not tested
LIGNIN QUALITY		partially acetylated ligning with some residual carbohydrates. Purity ~91%	very pure (>95%) and ash-free lignin, with a relatively low molecular weight and polydispersity
APPLICATIONS	cellulose pulp	general: paper pulp, cellulose- and glucose-derived chemicals	general: paper pulp, cellulose- and glucose-derived chemicals
		in BIOCORE: ethanol, itaconic acid	in BIOCORE: ehtanol, itaconic acid
	lignin	general: aromatic chemicals, performance materials, energy	general: aromatic chemicals and performance materials, energy
		in BIOCORE: phenolic resin, polyurethanes, polyesters	in BIOCORE: oxygenated aromatics, phenolic resin, polyurethanes, polyesters
	hemicellulose-rich fraction	general: animal feed (molasses), xylan- and xylose-derived chemicals, acetic acid, biogas	general: xylan- and xylose-derived chemicals, acetic acid, biogas
		in BIOCORE: xylose, ethanol, xylitol	in BIOCORE: furfural, furans

APPLICATIONS FOR ORGANOSOLV LIGNIN; THE BIOCORE PROJECT

Organosolv lignins can be used as a functional high-quality additive in inks, varnishes and paints. Other examples are the use in blends with polyethylene oxide, as radical scavenger (anti-oxidant) and as matrix material in biobased composites. Organosolv lignin is also a candidate for high-value applications such as carbon fibres and aromatic (specialty) chemicals. For the latter application the lignin should in general be depolymerized by appropriate technology such as chemocatalytic depolymerization, partial oxidation or pyrolysis. Finally, the high-quality organosolv lignin is a preferable candidate for phenolic resins and polyurethane (PU) foams. In the European 7th framework project 'BIOCORE' (Biocomodity refinery, 2010-2014 **[9]**) lignin was considered as a potential source of higher level revenues (compared to cellulose). Organosolv lignin was successfully applied by BIOCORE partner SYNPO (Czech Republic) as a solid co-polyol for the solvent-free production of castor oil-based polyurethane (PU) elastomers **[10]**. BIOCORE partner IWC (Latvia) successfully demonstrated the application of lignin as a liquid co-polyol for rigid PU foams **[10]**. In both cases PU's containing up to 30 wt% of lignin could be prepared. In general, PU's are among the most versatile plastic materials known and form the basis of many consumer products, insulating panels, shoes (soles), mattresses, toys, kitchen sponges … Depending on the nature of the components used, the PU can take the form of rigid or flexible foam, or that of elastomer-type plastic.

Also in BIOCORE, CHIMAR (Greece) has shown that organosolv lignin can be used to directly substitute up to 50 wt% of phenol in the preparation of PF resins for the manufacture of plywood panels **[10]**. In general, resins made from phenol and formaldehyde (PF-resins) are the major adhesives used to bind wood, creating products such as moulded products, lumber, timber products and panels such as plywood, particleboard, medium density fiberboards etc., which in some cases will be specifically designed to resist outdoor use conditions. These three BIOCORE examples show that products that valorize lignin are valuable features of higher performance product portfolios. In summary, the BIOCORE project addressed the efficient production and utilisation of fractions produced from lignocellulosic biomass by the CIMV acetic acid/formic acid process **[6,7]**. For comparison purposes, the ECN ethanol/water organosolv technology **[8]** was used as a benchmark. Multiproduct manufacturing value-chains were developed in BIOCORE and sustainability and benefits for the whole of society were demonstrated.

COMPARISON CIMV AND ECN

The CIMV acetic acid/formic acid and the ECN ethanol/water organosolv processes were studied in the BIOCORE project as two representative examples of organosolv fractionation. **Fig 1** presents a schematic overview of both processes as executed on pilot/lab-scale. Both organosolv processes were thoroughly compared based on experimental and Aspen Plus modelling results **[10]**. **Table 2** presents a qualitative comparison of the two organosolv processes. It is clear that the overall performance of both organosolv fractionation processes is roughly similar despite the differences such as the incorporation of pulp purification in the CIMV process which was not included in the ECN process. Also in the current operation the CIMV process is continuous, while the ECN process is batch-wise at bench-scale.

While the CIMV organic acid process is more suitable to produce sugars from the hemicellulose fraction and yields a more pure cellulose pulp (due to additional delignification step using H_2O_2), the ethanol organosolv process yields lignin with a higher purity. Both processes clearly show a good potential for use in lignocellulosic biorefineries. ❑

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