PROCESS DEVELOPMENT FOR PRODUCTION OF BIOFUELS FROM PAPER SLUDGE VIA FERMENTATION AND CHEMO-CATALYTIC CONVERSIONS

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ABSTRACT: The aim of the project "More Fuels from Organic Residues" (MOTOR) is to produce advanced biofuels for the transport sectors where electrification or gaseous biofuels will not generate the reduction of their carbon footprint in the short term. In MOTOR, wet lignocellulosic waste streams that do not compete with the food/feed market are used as a feedstock for a smart fermentation process. In the present study, the utilization of paper sludge as substrate for fermentation for production of fuel precursors and subsequent catalytic conversion to fuels at laboratory scale is described. The steps of the process were assessed experimentally, and based on the data generated, a conceptual process is being developed to explore the economic and sustainability aspects of the new value chain for biofuel.. Results show that solubilization of sugars from paper sludge using existing enzyme cocktails is very limited and needs improvement. On the other hand, the catalytic production of fuel from the fermentation products shows promising results in terms of type of products.
Keywords: biofuel, fermentation, lignocellulosic sources, chemo-catalytic conversion, conceptual process design

1 INTRODUCTION

According to the Paris Climate Agreement (2015) the global warming needs to be restricted to 2 ºC to prevent climate change. As a result the EU aims to reduce the emission of Greenhouse Gases (GHG) in 2050 with 80-95% relative to the 1990 reference year. In the transport sector, the aim is to reduce GHG emission with 60% concurrently with a reduction in fossil fuels consumption. Therefore, the long haul heavy duty automotive, marine and aviation transport sectors are investing in more efficient engines and the use of liquid biofuels. Current projections are that electricity and hydrogen, albeit coming from renewable resources, will only be marginally employed in these sectors.

The aim of the project " More Fuels from Organic Residues" (MOTOR) is to produce advanced biofuels for the hard to abate transport sectors where electrification or gaseous biofuels will not generate the reduction of their carbon footprint in the short term. Of special interest is the production of sustainable air fuel (SAF). Conventional aviation fuel is a mixture hydrocarbons with chain lengths between C7 and C17, with C11 being the most abundant component [1]. In MOTOR, by a smart process using wet lignocellulosic waste streams that do not compete with the food/feed market as a feedstock, fuels are produced that could be an addition to the current advanced biofuels. As model biomass, paper sludge, being a waste stream of a paper recycling facility in The Netherlands is used.

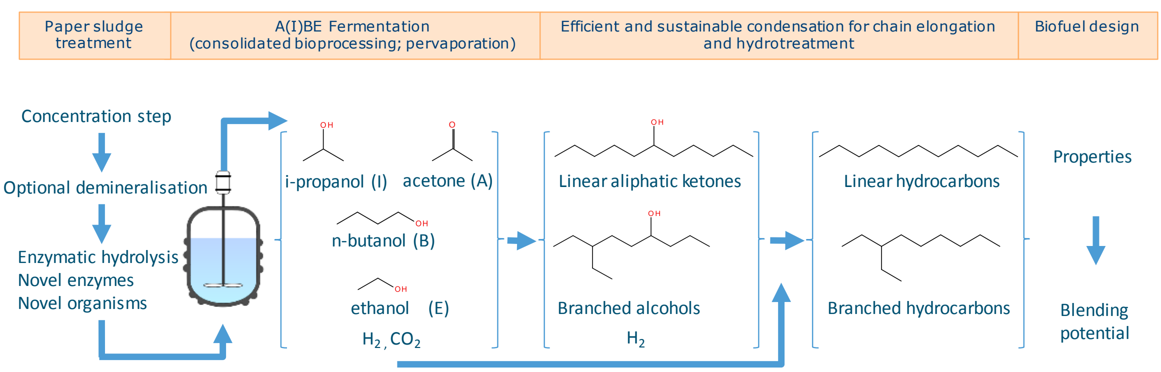

Figure 1: Approaches in MOTOR for valorization of paper sludge and 2nd generation biomass to biofuels

2 APPROACH

In MOTOR innovations are combined to make a breakthrough in producing a biofuel from 2nd generation biomass (Fig.1). The most important innovations are:

1. Use of paper sludge as a source for production of IBE (a mixture of isopropanol, butanol, ethanol) where bacteria are transformed to enable direct utilisation of cellulose by consolidated bioprocessing (no need of external enzymes)
2. Smart downstream processing is performed by thermo-pervaporation and extraction
3. A heterogeneous catalytic process is applied for formation of long chain aliphatic ketones from the IBE.
4. The aliphatic ketones are hydrotreated into iso-paraffins with hydrogen produced in the fermentation and ketone formation step, to make them applicable as hydrocarbon component in diesel fuel or jet fuel.

The MOTOR project aimed at making an early assessment study of the potential of this concept with experimental work on the main conversion steps, combined with a technical assessment for a full scale conceptual process design.

3 EXPERIMENTAL

3.1 Analysis of paper sludge

The biochemical composition of paper sludge was carried following a modified version of the NREL standard biomass analytical procedures [2-3]. In short, the content of lignin and carbohydrates was determined following hydrolysis in two steps: (1) 12 M (72% w/w) H_2SO_4 (30 °C, 1 h) and (2) 1.2 M H_2SO_4 (100 °C, 3 h).

The solid residue was determined gravimetrically and its ash content was measured. The acid-insoluble lignin content was based on the amount of ash-free residue, and acid-soluble lignin was determined using UV–VIS absorption. Finally, the hydrolysate was analysed for monomeric sugars. Ash content was determined according to the standard NREL procedure.

Monomeric sugars were analysed by High-Performance Anion Exchange Chromagraphy (HPAEC)-PAD (ICS3000, Dionex) equipped with a CarboPac PA1 column and a post column addition of 0.2 mL/min 0.25 M NaOH. A gradient of NaOH was used as eluent (0.25 mL/min): 15 mM (0–1 min), 0 mM (1–21 min), increasing from 0 to 187.5 mM (21–37 min), 250 mM (37–42 min), decreasing from 250 to 15 mM (42.0-42.1 min) and 15 mM (42.1-50 min). Lactose was used as an internal standard. Samples with acidic pH were neutralised with barium carbonate and centrifuged before analysis.

3.2 Microorganisms and cultivation conditions

Clostridium beijerinckii B593 is a laboratory strain. Strain was kept as spore suspension at -20°C. Preparation of cultures was performed as described in [3]. Cultures were statically incubated at 37 °C. The medium used contained (per L) KH_2PO_4 1g, K_2HPO_4 0.76 g, CH_3COONH_4 2.9 g (of which CH_3COO^- is 2.2 g), yeast extract (Duchefa) 2.5 g, $FeSO_4.7H_2O$ 6.6 mg, $MgSO_4.7H_2O$ 1 g, and p-aminobenzoic acid (p-ABA) 0.1 g. Glucose was added to the hydrolysate at 10 g/L, as indicated. Analysis of metabolites and sugars was performed as previously described [3].

3.3.Chemical reactions

Chemocatalytic conversion of IBE into long-chain precursors was done in a one-pot batch conversion screening various catalyst. The IBE obtained from fermentation was dissolved in heptane solvent. Samples were analyses using gas chromatography analysis.

Hydrogenation of the aliphatic ketones was evaluated in a autoclave gas/liquid batch screening study at temperatures between 150-230°C and pressures 30-50 barg applying various calyst/support combinations. Both real mixtures from the chemocatalytic precursor synthesis as well as synthetic mixtures were used, where in both cases the precursors were dissolved in heptane solvent. Samples were analyses using gas chromatography analysis.

4 PAPER SLUDGE COMPOSITION

Samples of paper sludge from a recycling paper facility were supplied by Smurfit Kappa. The composition in terms of sugars, ash and lignin is shown in Table I.

Table I: Composition of paper sludge used in this study.

Component	% of dry matter
Glucan	16.4
Xylan	2.5
Other sugars	2.4
Total lignin	16.7
Ash	55.5

5 FERMENTATION OF PAPER SLUDGE STREAMS

The conversion of sugars in paper sludge (PS) hydrolysate to a mix of isopropanol, butanol and ethanol (IBE) was carried out by *Clostridium beijerinckii*. The soluble sugars in the PS-medium were converted into IBE (Fig 2). Both monomeric glucose and xylose were consumed and an IBE mix was produced at yield higher than 0.3 gIBE/g sugar consumed, indicating that other sugars or oligosaccharides in the hydrolysate were consumed.

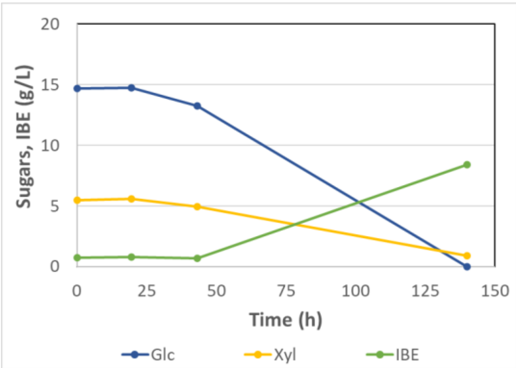

Figure 2: Production of isopropanol, butanol and ethanol (IBE) by Clostridium beijerinckii on PS-hydrolysate supplemented with glucose (10 g/L). Abbreviations: Glc, glucose; Xyl, xylose.

6 LONG CHAIN ALIPHATIC FUEL COMPONENTS FROM IBE

Long chain aliphatic ketones were produced from a synthetic mixture of IBE in heptane using heterogeneous catalysts. Various catalyst/support combinations were screened for optimal conversion and product distribution characteristics. C7-to-C15 components were obtained with selectivity towards C11-C15 chain lengths at a temperature of 145°C and autogeneous pressure. A typical product distribution is depicted in Fig. 3.

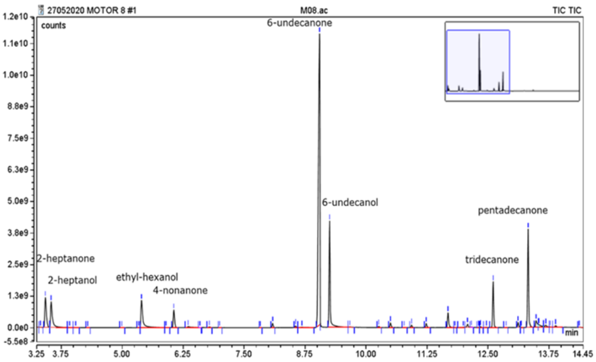

Figure 3: Product distribution of IBE conversion to aliphatic ketones

Full conversion (>95%) of the ketones an alcohols in a synthetic mixture was demonstated using a supported noble metal catalyst. The product was found not to contain significant amounts of by-products and no significant formation of coke was observed.

7 CONCEPTUAL PROCESS DESIGN

The feedstock used for the MOTOR process is a paper sludge waste stream from a paper recycling mill, but the concept can be applied to other cellulose-containing streams as well, including those from 2nd generation biorefineries. The process flow diagram developed is depicted in Fig. 4.

The feed stream of paper sludge can optionally undergo demineralisation/detoxification. In the base scenario this was not implemented. The resulting stream is sterilized (not depicted) and fed to a (fed) batch fermenter. The resulting stream undergoes a simultaneous consolidated bioprocessing approach (CBP) using a strain of *C.beijerinckii*. In particular, the cellulose in the paper sludge is hydrolysed by enzymes produced by the microorganisms, and the resulting sugars are fermented to IBE. The fermentation product is filtrated to remove the biomass. The diluted aqueous IBE stream is first fed to a membrane pervaporation step to produce a concentrated aqueous IBE stream and an organic IBE stream. The permeate stream contains approximately 50w% water from which the IBE is further separated by extraction with hexane that also serves as the solvent required by the downstream process.

The IBE is converted into linear aliphatic ketones (C7-C15) using a heterogeneous catalyst. The solvent is recovered from this stream by distillation and is recycled. The aliphatic ketone stream is then hydrotreated in the presence of a heterogeneous catalyst to obtain linear and branced alkanes. The hydrotreatment step utilises H_2 produced in the fermentation as well as in the dehydrogenation step. Both streams contain small amount of organics and especially the stream from fermentation contains a large amount of CO_2. Pressure swing adorption (PSA) was selected to purify the H_2 up to the hydroganation feed specifications.

Finally, the linear alkane product stream is purified in by distillation. The product is a sustainable aviation fuel SAF stream suitable for blending to obtain the required SAF specifications.

The process was modelled in the flow sheeting tool Aspen Plus, where experimental data were translated into full industrial scale, fully developed technology. Results show that the SAF product stream consists of C7-C15 stream predominantly consisting of linear C11 and branched C8 alkanes. The share in of C11 product could potentially be increased by increasing the amount of isopropanol obtained from fermentation. The mass yield in cellulose to SAF is 13%. Losses were found to be mostly in the fermentation, filtration and membrane separation steps. This becasue of respectively fundamental limitation in the reaction stoichiometry, and in the conservative estimation of the conversion and fundamental limitations in membrane separation. The losses in extraction, and conversion in alkanes were found to be relatively low.

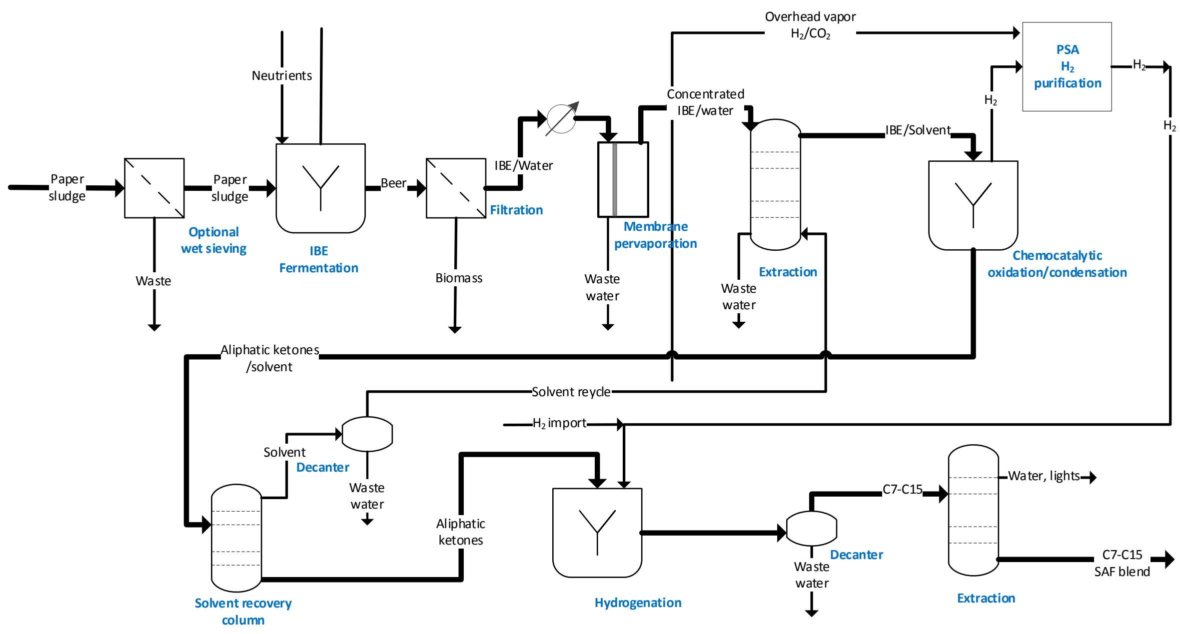

Figure 4: Process flow diagram of the MOTOR process.

8 CONCLUSIONS

- Paper sludge is a recalcitrant feedstock for saccharification using enzymes. Salts and other components might need to be removed before saccharification and fermentation.
- Chemical catalysis of the fermentation products yields aliphatic compounds in range of C7-C15, with predominantly C8 and C11.
- Near full conversion was obtained for the aliphatic ketones and alcohols produced using a supported noble metal catalyst.
- A conceptual process design was made for the process including calculation of mass and heat balances of the process were developed for evaluation of the feedstock to fuel efficiency and to assess the quality of the fuel stream. The theoretical carbon efficiency in the IBE fermentation, the limited losses in IBE purification and the carbon efficiency in the chemo-catalytic conversion step. Further improvement of the latter step as well as tailoring the ratio of isopropanol/butanol/ethanol in the IBE stream are important for further optimization.

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