A Norwegian steam explosion biorefinery

Størker T. Moe,[1*] Dag Helge Hermundsgård,[2] Mihaela Tanase-Opedal[3], Rune Brusletto[4]

[1] Norwegian University of Science and Technology (NTNU), Trondheim, Norway
[2] University of Bergen (UiB), Bergen, Norway
[3] RISE PFI AS, Trondheim, Norway
[4] Arbaflame AS, Oslo, Norway

ABSTRACT

The ArbaOne biorefinery located in eastern Norway uses a patented steam explosion process for co-production of "brown" biofuel pellets and furfural. The plant is the first of its kind, and challenges were encountered during the startup phase. Most of these challenges are now handled, and further work to extend the product portfolio is ongoing.

KEYWORDS

Steam explosion, Softwood, Solid biofuel, Furfural, Furaldehydes

INTRODUCTION

Furfural is a bio-based heterocyclic aromatic aldehyde. It is produced industrially by steam treatment of acidified xylan-rich raw materials, typically corn cobs or sugarcane bagasse.[1] The world production is estimated to approximately 300 000 tons/year, with China, The Dominican Republic, and South Africa as the major producers. The main applications for furfural are as a raw material for furfuryl alcohol and as a selective solvent.[2] Furfural is also an effective fungicide and nematocide [1] and has been used as a rocket fuel component.[3] It is now regarded as a very promising platform molecule for bio-based chemicals.[2,4] During the production of furfural, several byproducts are formed due to the multitude of side reactions in the reactor.[1] The most notable side reactions are:

- Deacetylation of hemicelluloses, forming acetic acid
- Hydrolysis of non-cellulosic polysaccharides, forming oligo- and monosaccharides
- Acid dehydration of pentoses forming furfural
- Acid dehydration of hexoses forming 5-HMF
- Acid dehydration of 6-deoxyhexoses forming 5MF and 2AF [5]
- Methanol formation
- Degradation of 5-HMF, forming levulinic acid and formic acid
- Degradation of coniferaldehyde groups on lignin, forming acetaldehyde
- Radical coupling of acetaldehyde, forming 2,3-butanedione

5-HMF has seen considerable interest in the recent years due to its properties as a platform chemical, but the current world production is limited.[6]

After the steam treatment of the acidified raw material, the vapor from the reactor is collected, condensed and distilled to yield furfural of the required purity. Normally, furfural distillation takes place in two stages. In the so-called azeotrope column, light boilers are taken out as top distillate, a furfural/water mixture containing 15-20% furfural is taken out as a side draw, and the bottom fraction contains the less volatile components in the distillate (typically acetic acid and formic acid). The furfural/water vapor is condensed and decanted to yield a furfural-rich organic phase and a furfural-lean aqueous phase. The aqueous phase is recycled to the azeotrope column, while the organic phase is distilled at reduced pressure in the furfural column. In this column, high-purity furfural is taken out close to the bottom, while the top distillate is recycled to the decanter.[1]

Steam explosion pretreatment of lignocellulose was first introduced in 1926 for fiberboard production.[7-9] Later, steam explosion has been suggested as a method for producing fermentable sugars from wood,[10] for mechanical pulp production[11,12] and as a pretreatment process before enzymatic hydrolysis of lignocellulosic biomass.[13,14] Steam explosion is also used for pretreatment of organic waste before biogas digestion.[15,16]

Steam pretreatment of lignocellulose with low moisture content is used for the production of so-called "brown" biofuel pellets,[17,18] and these pellets have superior properties compared to conventional "white" wood fuel pellets.[19]

THE ARBAONE BIOREFINERY

The ArbaOne biorefinery is located in Grasmo outside Kongsvinger in Eastern Norway. The plant is fully owned by Arbaflame AS and started up in the 4th quarter of 2020. The ArbaOne plant uses a patented[17,18] steam explosion process to co-produce "brown" biofuel pellets and furfural. Figure 1 shows the process layout of the pellet line, and Figure 5 shows the process layout of the furfural line.

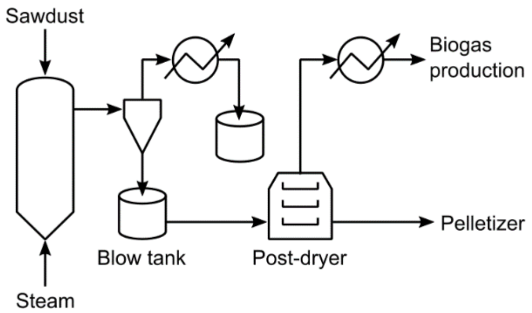

Figure 1. Simplified flowsheet of the pellet line at ArbaOne. The pre-dryer before the steam explosion reactors and the separation of non-condensable gases after the condenser have been omitted from the flowsheet.

After pre-drying to 30-45% moisture content, the biomass (softwood sawdust) is filled into one of the four steam explosion reactors. Process steam is injected at the bottom of the reactor to reach a temperature of 200-300 °C. After a predetermined cooking time, the reactor is emptied through a pipe to a cyclone separating the solids and the vapor. The vapor is taken to a condenser, while the solids are collected in the blow tank. The solids are then transported from the blow tank to the post-dryer and dried in the post-dryer before pelletizing.

The condensate from the post-dryer is sent to an anaerobic wastewater treatment system producing biogas which is used onsite for production of steam. The dried biomass contains the non-volatile reaction products from the steam explosion process.

Compared to conventional (“white”) biofuel pellets, the brown pellets are more brittle, more hydrophobic and with a lower content of volatile matter, making them better suited as a substitute for mineral coal in boilers.

Figure 2. Biofuel pellets produced at the ArbaOne plant.

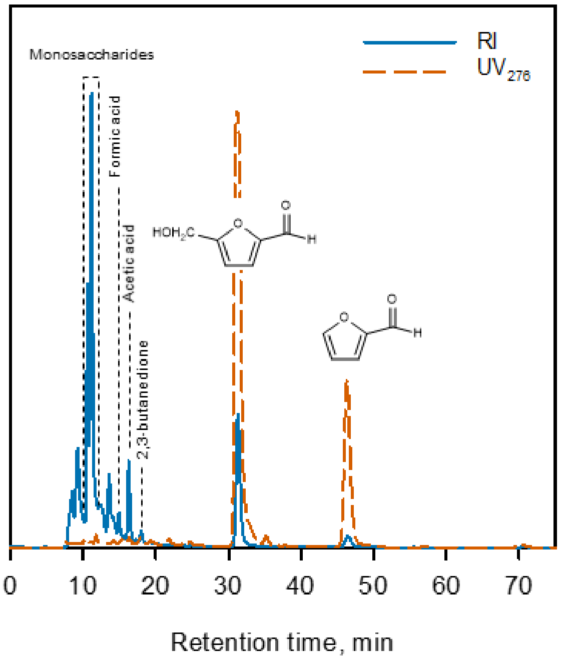

Figure 3. HPLC-UV-RI chromatogram of a biomass leachate sample. Agilent Hi-Plex H, 50 mM H_2SO_4.

The liquid phase in the steam exploded biomass contains some of the volatile reaction products, and the non-volatile reaction products. A chromatogram of a leachate sample is shown in Figure 3.

After the condenser, the non-condensable gases are fed to the steam boiler. The condensate is transferred to a skimming tank for removal of volatile extractives and then ultrafiltered before it is stored in the condensate tank.

The condensate from the steam explosion reactor contains up to ~25 g/L furfural, making it toxic for micro-organisms [20,21] and thus unsuitable for treatment in a biological wastewater treatment plant. Although the furfural concentration is lower than the concentrations encountered in condensates from furfural production reactors,[1] it is high enough for economically viable purification.

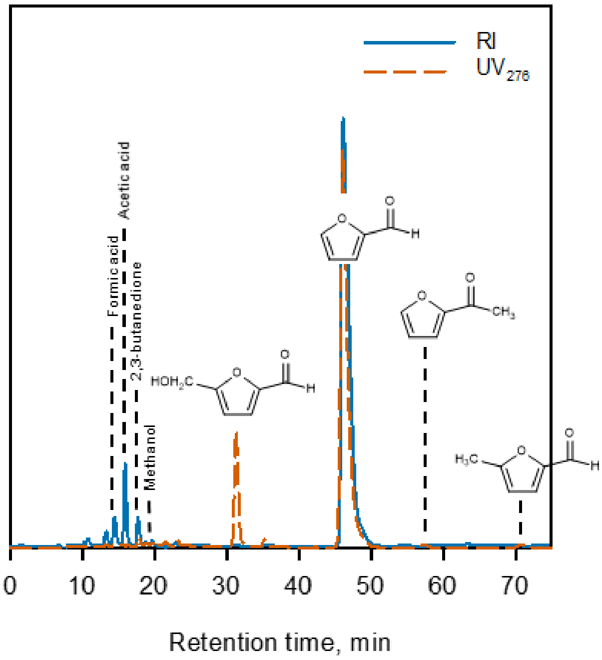

Figure 4. HPLC-UV-RI chromatogram of a steam explosion condensate sample. Agilent Hi-Plex H, 50 mM H_2SO_4.

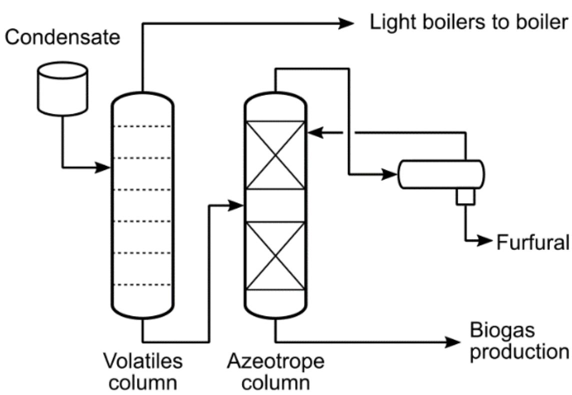

Figure 5. Simplified flowsheet of the furfural line at ArbaOne. Condensate skimming and filtration, heat exchangers, reboilers and condensers have been omitted from the flowsheet.

In the ArbaOne biorefinery, the first stage of furfural purification is performed in two conventional distillation columns instead of in one column with a side draw. In column 1 (the volatiles column), the light boilers (methanol, acetone, 2,3-butanedione) are taken out as the top distillate and used directly as a fuel in the steam boiler. In column 2 (the azeotrope column), a furfural/water mixture with a composition close to the azeotropic point is taken out as top distillate. The bottoms fraction contains predominantly acetic acid, formic acid and water. The bottoms fraction is sent to the anaerobic wastewater treatment system to produce biogas for use onsite. The top distillate is decanted into one furfural-rich organic phase and one furfural-lean aqueous phase. The aqueous phase is recycled to the azeotrope column. The organic phase from the decanter is not purified further, and the raw furfural (~90% purity) is sold for purification offsite.

STARTUP CHALLENGES

The plant is the first of its kind, and several process solutions were of new design. The most prominent deviation from traditional furfural purification was the choice of using two distillation columns to separate light boilers, furfural azeotrope and wastewater instead of the traditional single column with a side draw.[1]

After some time, large amounts of black particles were observed in the furfural line, causing scaling in pipes and clogging of sieves. The particles were virtually insoluble in any solvent tested, and it was concluded that they consisted of a cross-linked polymer.

Pyrolysis-GC-MS analysis of the particles indicated the presence of both wood extractives and furan structures. In laboratory experiments, addition of wood extractives did not induce formation of solids in steam explosion condensate samples upon heating. However, addition of sufficient amounts of furfural to form an organic phase induced polymerization.[22] It was concluded that the particles consisted of a furfural polymer, with extractives either absorbed in the particles or co-polymerized with the furfural.

The distillation columns were simulated in Aspen HYSYS, and the calculated concentration profiles of the two columns is shown in Figure 6. As can be seen from Figure 6a), the furfural concentration is above the solubility limit in water and close to the azeotropic point in the upper region of the volatiles column, and the furfural may percolate in the high-concentration region before finally exiting the column with the bottoms fraction. At these furfural concentrations, the liquid phase may phase separate and form a furfural-rich organic phase. The conditions are thus favorable for the formation of solids. The problem was exacerbated by the azeotrope column output being recycled to the condensate tank during periods when the steam explosion process wasn't running. Revised operational protocols where the column outputs weren't recycled to the condensate tank eliminated the formation of polymer particles.

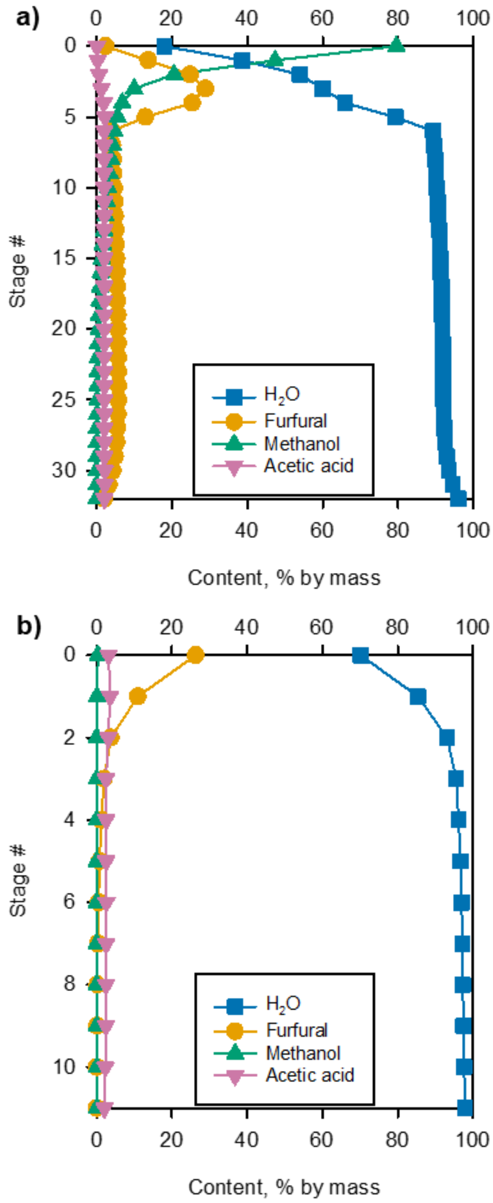

Figure 6. Concentration profiles of **a)** the volatiles column and **b)** the azeotrope column. Simulation in Aspen HYSYS 12.1 using the UNIQUAC property package.

During the spring of 2022, the anaerobic wastewater treatment plant encountered problems. Accumulation of volatile fatty acids and reduced methane content in the biogas indicated inhibition of the methanogens. Analyses of the post-dryer condensate fed to the biogas plant showed furfural concentrations of up to 8 g/L, in excess of the concentration expected from the vapor-liquid equilibrium of furfural-water mixtures. As furfural is known to inhibit microbial growth,[22,23] the reduced performance in the wastewater treatment plant was attributed to the concentration of furfural in the post-dryer condensate. The difference between the theoretical equilibrium concentrations and the observed concentrations was attributed to mass transfer limitations.

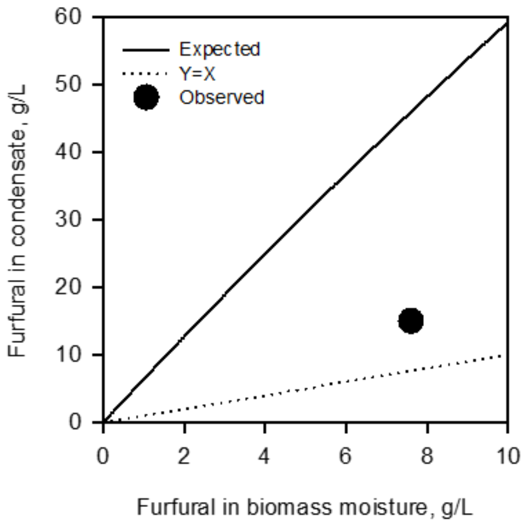

Figure 7. Expected vs observed furfural concentrations.

Currently, various process modifications are investigated to recover furfural also from the post-dryer condensate to improve furfural recovery and reduce the load on the wastewater treatment plant.

OUTLOOK

The liquid phase in the steam exploded biomass contains significant concentrations of mono- and disaccharides, 5-HMF and furfural. Washing the biomass will reduce the levels of furans in the biomass, removing furfural and carbohydrates from the post-dryer condensate. The furans can be recovered from the filtrate by liquid-liquid extraction. If 5-HMF and furfural can be successfully isolated from the extractant, the furfural yield will be improved and 5-HMF as a new product may constitute an additional revenue stream for the plant.

The extracted wash filtrate contains sufficiently low levels of furaldehydes to make it suitable as a fermentation substrate for production of *e.g.* single cell protein for animal feed.

The steam explosion condensate contains not only furfural, but also other compounds which may increase the revenue for the plant if they can be successfully isolated in sufficient purity. The most notable compounds are 2,3-butanedione and 5-methyl furfural which can be used as flavoring compounds.

CONCLUSIONS

After some startup challenges, co-production of high-quality biofuel pellets well suited as a replace-ment for fossil coal, and furfural has been successfully demonstrated in production scale. The steam explosion biorefinery has a potential for extending its product portfolio for increased revenue.

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