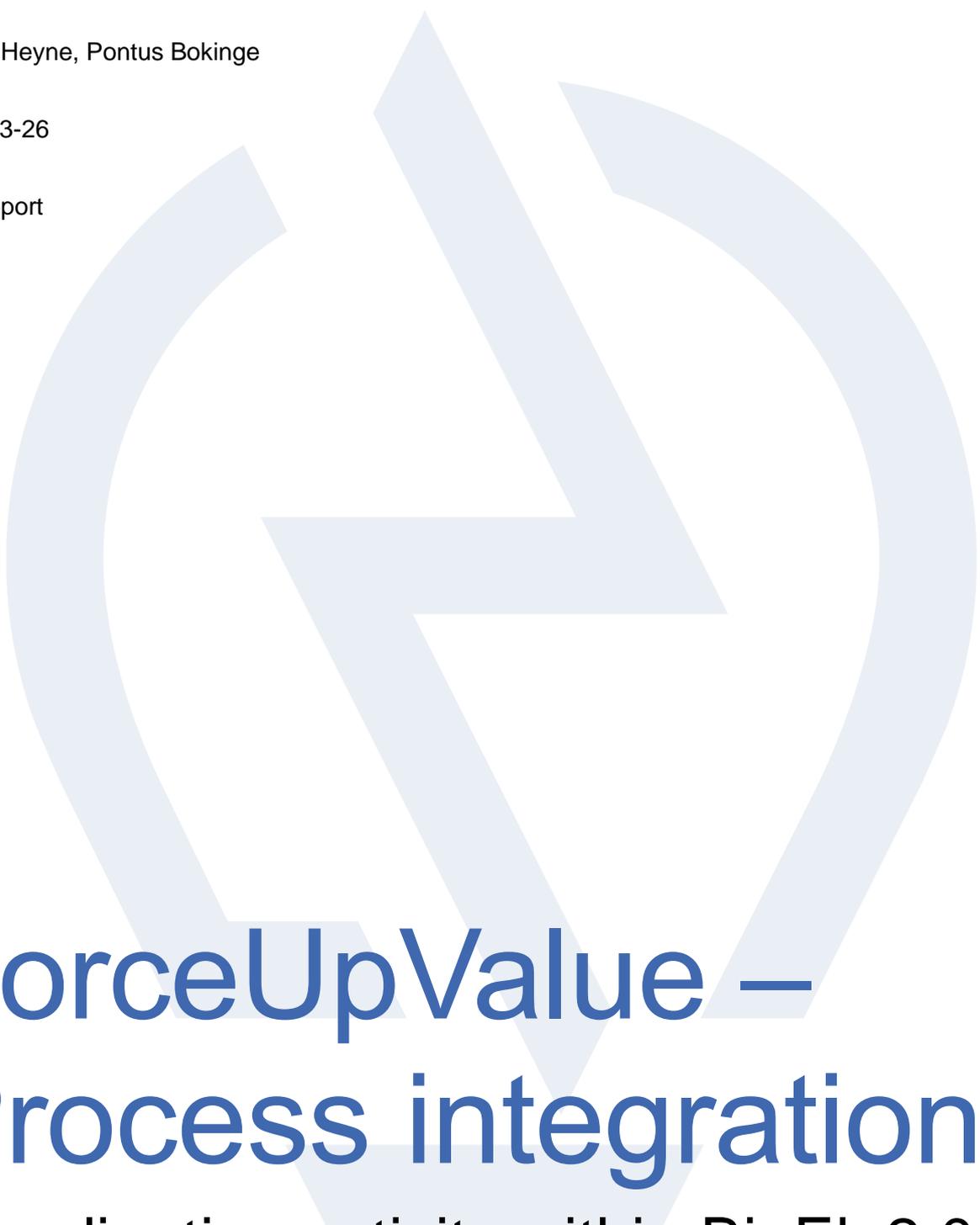


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ForceUpValue – Process integration

Coordination activity within BioEk 2.0

Summary

Within the framework of the innovation project *BioEkonomi 2.0 – Bättre valorisering av restströmmar* (BioEk 2.0) several coordinating activities were conducted giving all sub projects the opportunity to participate. The present report summarizes the results of the coordinating activity ”process integration” working towards the sub project *ForceUpValue – Prebiotika från skog och hav*.

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1 Background

Within the project *ForceUpValue* the production of prebiotic cello-oligosaccharides (COS) from non-edible resources is investigated. Both marine and forest-based feedstock for production of this type of functional food is investigated in order to mobilize processing synergies for the raw material streams that can strengthen both technology deployment as well as the product development. This finally aims at improving opportunities for commercialization.

Within the framework of the coordinating activity *Process integration* the focus is on specific opportunities for material and energy integration of the processes developed within *ForceUpValues*. This implies integration with existing industry infrastructure or potential biorefinery concepts in order to maximize the overall energy and resources efficiency. Given the existing data sets and the budget/time restrictions the process integration study focused on the forest-based COS production and its integration to a biorefinery concept.

2 Process description

2.1 ForceUpValue

The focus of the process integration study is on forest based COS production based on the flow scheme illustrated in figure 1, also indicating mass yields and by-products generated during production of COS. From 1 kg of birch, 62.7 g of COS are produced by pretreatment with the newly developed advanced organosolv technology, separation of the cellulose-rich stream and enzymatic treatment. COS is a high-value product that – based on mass flow – only makes up a minor part of the total of product streams generated. There is a stream rich in hemicellulose (Xylose fraction in figure 1), a lignin fraction, as well as the remaining stream rich in cellulose after production of COS. All these streams can be refined to numerous products in different ways.

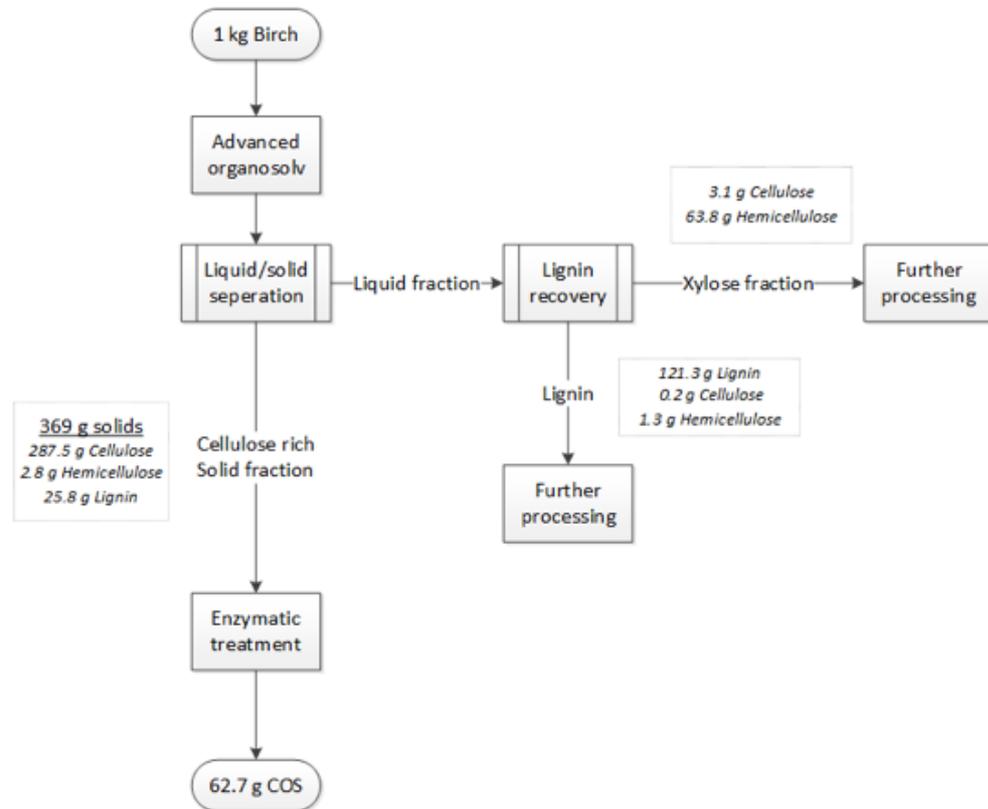


Figure 1: COS production from forest biomass – mass yields and composition.

2.2 Forest based biorefinery

In order to enable economically viable large-scale production of COS from forest biomass, it is important to identify value-added products that can be produced from the above-mentioned remaining side-streams. There is a large spectrum of different biorefinery concepts leading to various possible products, such as:

- fuels
- building material
- textiles
- chemical intermediates
- pharmaceuticals and medical products
- food products and additives
- paint and dye
- hygiene products

The complexity of biorefinery value chains is also illustrated in figure 2 where basically all products mentioned in the bottom can be obtained by using lignocellulosic feedstock in form of crops or residues.

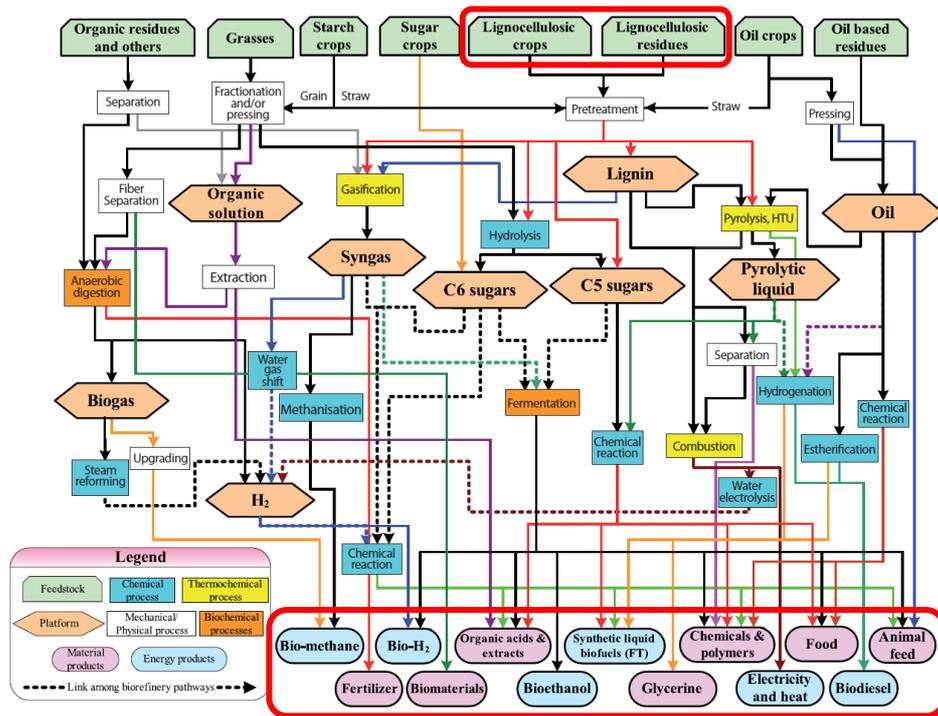


Figure 2: IEA Task 42 - Biorefinery classification scheme [1].

A forest-based biorefinery concept that has been studied extensively – and that also is available at commercial scale – is forest-based ethanol production. The concept generates several by-products such as biogas, lignin and carbon dioxide.

For the present study forest-based ethanol production has been chosen for integration of COS production. A main reason for choosing that process concept is the existence of studies based on the organosolv pretreatment that can be used as basis for the evaluation ([2], [3]). The biorefinery concept evaluated within this study is illustrated in figure 3. Products generated – in excess of COS – are ethanol and pyrolysis oil, as well as, if possible from an energy integration perspective, biogas.

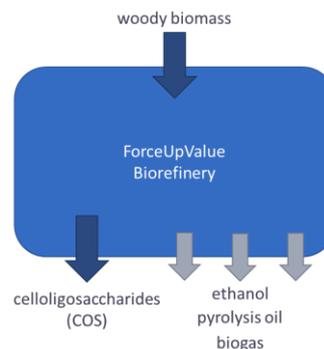


Figure 3: Forest-based COS production with by-products generated from side-streams.

It is based on the techno-economic evaluation of advanced organosolv for ethanol production by Mesfun *et al.* [2]. The case for softwood with conversion of both cellulose and hemicellulose streams to ethanol (referred to as “SWBF” in [2]) is used as starting point. The following modifications and adjustments are made to the process concept:

- production of COS is introduced based on the cellulose-rich stream after filtration and prior to simultaneous saccharification and fermentation (SSF), no energy demand for separation of COS from the remaining cellulose stream for SSF for ethanol production is accounted for
- The separated organosolv-lignin is assumed to be further converted to pyrolysis oil as a marketable product. The yields and energy demands are based on Kalogiannis *et al.* [3]
- Biogas production from the wastewater treatment plant and other remaining side streams is accounted for. The biogas yield from the organic matter is based on data from Humbird *et al.* [4]
- A biomass dryer is introduced to bring the incoming biomass (assumed at 50 wt-% moisture content) to the feedstock moisture content (6 wt-%) used in the study by Mesfun *et al.* [2].

3 Process integration

In the present section the mass and energy balances are given for a base case (case A) process integrating the COS production to the ethanol production process via advanced organosolv as described above. The scale of the process is $100 \text{ MW}_{\text{LHV}}$ of biomass as fuel input for production of COS, ethanol, lignin oil, and – if possible given the internal heat demand – biogas. In addition a case investigating an alternative ethanol make-up process being less energy-intensive is investigated in a “low energy case” (case B). As the advanced organosolv process represents a large energy sink in the overall process concept, a simplified sensitivity analysis investigating decreased liquid-to-solids ratio (LSR) is conducted as well.

3.1 Base case (case A)

For the base case the overall mass and energy balances are illustrated in figure 4. The following changes have been made in relation to the reference process taken from Mesfun *et al.* [2]:

Adjustments with respect to mass balance:

- The introduction of a COS reaction step leads to a reduced mass flow to the SSF step. The yield in the COS reactor is assumed to be 21 wt-% based on cellulose feed flow. The flow composition downstream the COS reactor has been adjusted assuming a consumption of 0.95 kg of cellulose and 0.05 kg of water per kg of COS. It is assumed that the introduction of a COS reactor does not affect the downstream units more than affecting the mass flows, so no additional changes occur.
- The production of lignin oil, coke and gas in the pyrolysis plant is based on experimental data for thermal pyrolysis of lignin from advanced organosolv published by Kalogiannis *et al.* [3]. The product distribution (based on kg/kg dry lignin) used is 0.474 kg of lignin oil, 0.395 kg of coke and 0.127 kg of pyrolysis gas. The incoming lignin is assumed to have a moisture content of 0.38 kg H₂O/kg wet lignin.
- The biogas yield in the wastewater treatment plant is based on a publication on cellulosic ethanol production from the National Renewable Energy Laboratory [4]. The produced volume of biogas is assumed to be linearly proportional to the mass flow of *soluble solids* entering the wastewater treatment (the weight fraction of soluble solids in the present concept is at 6.5 wt-% versus 5.7 wt-% in [4]).

Adjustments with respect to energy balance:

- Mesfun *et al.* [2] evaluate a process concept with incoming biomass at 6 wt-% moisture content. In the present concept biomass at 50 wt-% moisture content is assumed as feedstock, making the introduction of a biomass dryer necessary. The energy demand of the dryer is based on a model for low-temperature air drying based on Heyne and Harvey [5] with a specific energy demand of 3.312 MJ/kg H₂O evaporated.
- The solvent recovery for the advanced organosolv process is based on conventional evaporation as in the base case for Mesfun *et al.* [2].
- No energy demand is accounted for for the COS reactor due to limited data availability.
- The energy consumption for ethanol purification (using a sequel of for distillation columns in the base case) is assumed to remain unchanged even though total flow and concentration are changed to some extent with the introduction of the COS reaction step (decreased total flow and decrease of ethanol concentration after SSF from about 17 wt-% to 15 wt-%).
- The pyrolysis plant is assumed to have an energy efficiency based on the lower heating value of 70% based on [3]. The lower heating values of the relevant material streams to and from the pyrolysis plant are taken as:
 - o Lignin: 16.1 MJ/kg
 - o Lignin oil: 16 MJ/kg
 - o Coke: 26 MJ/kg
 - o Pyrolysis gas: 16.4 MJ/kg

The assumption on 70 % energy efficiency implies that all of the pyrolysis gas needs to be burnt internally to the pyrolysis plant in order to sustain the process. The flue gases from pyrolysis are assumed to be available for heat recovery to the process.

- Based on NREL [4] the biogas lower heating value is taken as 12.6 MJ/kg.
- The process cooling demand includes condensers in ethanol purification (four columns) as well as the cooling of the effluent from the pretreatment reactor (organosolv). All cooling demands are directly taken from Mesfun *et al.* [2].
- The potential for internal heat recovery (e.g. using process cooling demand at higher temperature to cover heating demand) has been determined using pinch analysis. The minimum interval temperature for heat exchange ($\Delta T_{\min}/2$) is assumed to be 10 °C for flue gases and the biomass dryer and 2.5 °C for the remaining streams. The remaining process heating demand is assumed to be covered by an internal steam boiler using internally produced biogas and coke as fuel at first hand, in case of large heating demand importing extra forest-based fuel. The energy efficiency of the boiler is taken as 0.85.

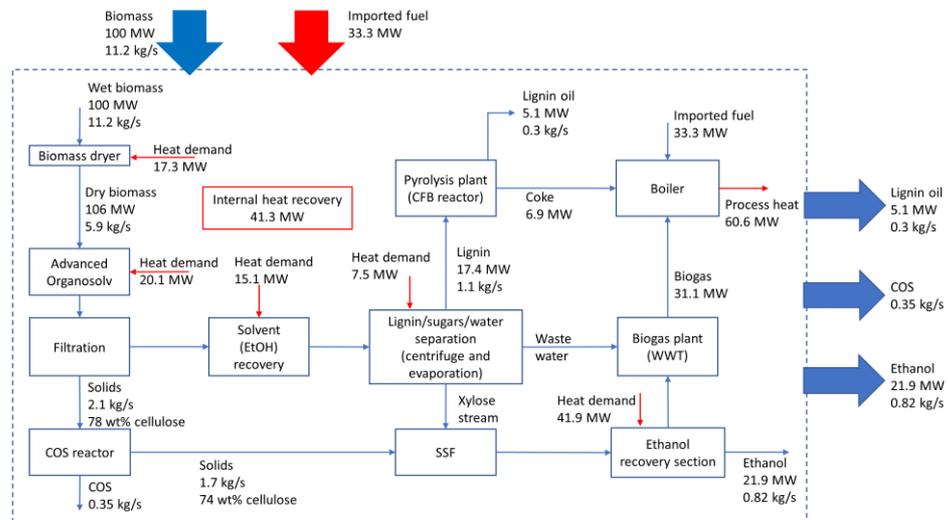


Figure 4: Mass and energy balance for base case (case A) generating COS, lignin and ethanol from forest biomass.

For the base case, all biogas and coke is burnt internally, even making an import of fuel ($33 \text{ MW}_{\text{LHV}}$) necessary. The major heat sinks within the process are the organosolv process and the associated solvent recovery section (amounting to 42.7 MW)– that is operating at a rather high LSR of 10 – , the ethanol purification section (41.9 MW) and the biomass dryer (17.3 MW). Internal heat recovery (41.3 MW) can cover part of that demand, though requiring all generated biogas to be burnt in the boiler. A Grand Composite Curve (GCC) illustrating the heat recovery as well as the minimum external heat demand of the base case is illustrated in figure 5.

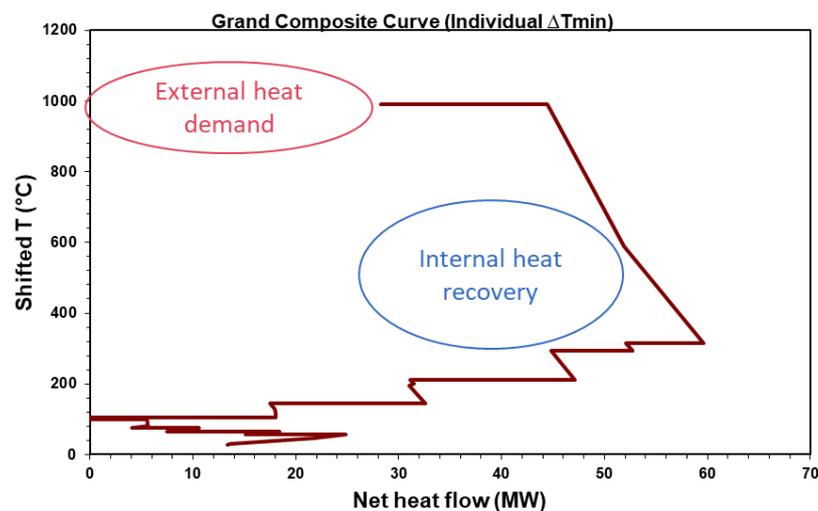


Figure 5: Grand Composite Curve for the base case COS production process (Case A).

3.2 Low energy case (case B)

For the low energy case (case B), the following two assumption on reducing the energy demand are made:

- the advanced organosolv process is run on a liquid-to-solid ratio (LSR) of 4 instead of 10, substantially reducing the energy demand for pretreatment, solvent recovery, as well as lignin/sugar/water separation by 60 %. The pretreatment efficiency with respect to cellulose yield and purity is assumed to remain unchanged. This is probably an overestimation of the organosolv efficiency, but due to lack of experimental data at lower LSR no well-founded estimations could be made.
- The ethanol purification was modified, using molecular sieves for the final upgrade instead of an extractive column; this reduces the thermal energy demand as well as the equipment used (two distillation columns replaced by molecular sieves). The reduced thermal energy demand is estimated based on data from NREL [4].

The mass and energy balance for case B is illustrated in figure 6. The heat demand reduction makes it possible to cover all heat internally without importing fuel, even allowing for an export of biogas of 8.1 MW. The internal heat demand still is dominated by the advanced organosolv process, the ethanol purification and the biomass dryer. The generation of products (COS, ethanol, lignin oil) remains unchanged as the processes are assumed to operate at similar conditions to the base case.

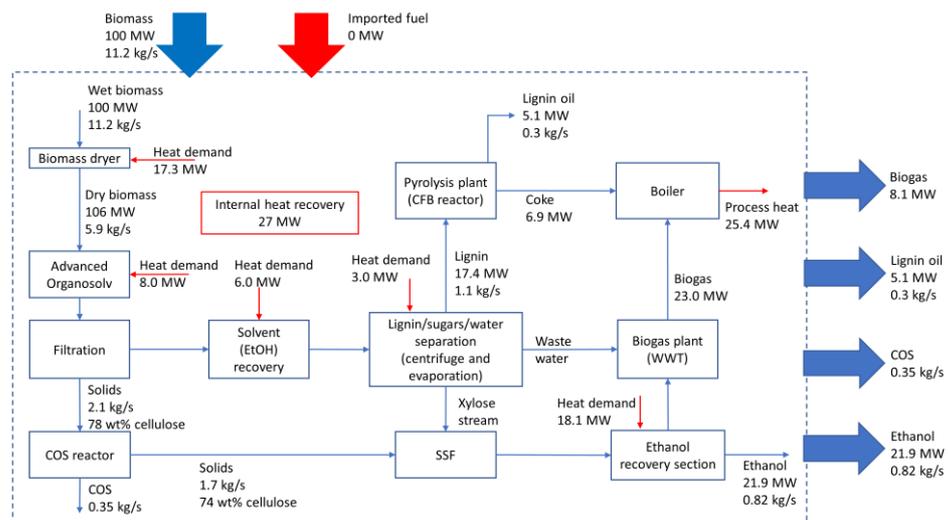


Figure 6: Mass and energy balance for low energy case COS production (case B).

The GCC for case B is illustrated in figure 7.

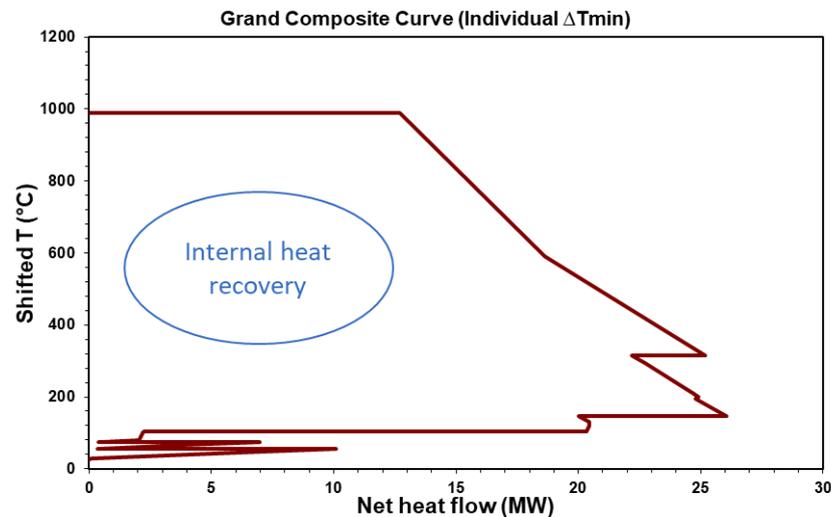


Figure 7: Grand Composite Curve for the low-energy COS production process (Case A).

3.3 Sensitivity analysis

Given that the advanced organosolv is the absolute dominant heat sink in the COS biorefinery concept evaluated, a sensitivity analysis on the influence of decreasing the LSR in the pretreatment was conducted. One aim was to analyze at what liquid-to-solid ratio (LSR) the process can be thermally balanced, meaning that all internal fuels generated are enough to supply heat to the process. For that case, no export of biogas is possible, but no additional external fuel supply is needed either.

Due to lack of data, no impacts on the fractionation performance of the advanced organosolv process has been accounted for in the sensitivity analysis but the impacts presented are only on the energy balances due to changed heat demands. A decrease in LSR will probably lead to decreased performance of the fractionation into cellulose and lignin/hemicellulose streams. But the high energy demand of the organosolv process needs to be reduced to make the process viable at large scale, as also pointed out by Mesfun *et al* [2]. Therefore a sensitivity on the thermal effects is of interest to identify at what LSR the process is thermally balanced.

In figure 8 the influence of LSR on the need for external energy supply or energy surplus (export of biogas), respectively, is illustrated for the COS biorefinery concept evaluated. The blue curve represents the base case with standard ethanol purification train, whereas the red curve represents the case of a more energy efficiency ethanol upgrade with molecular sieves.

It can be noted that – for the case of standard ethanol purification (blue curve) – external fuel import is always necessary, even at LSR as low as 3. For the improved ethanol purification, the process is thermally balanced at LSR of about

6.75. In order to export biogas, a lower LSR needs to be achieved. It must be kept in mind though that the fraction performance of the organosolv process has been assumed constant (at the base case value of LSR of 10), probably overestimating the overall process performance at lower LSR values. Figure 9 illustrates the mass and energy balance for the thermally balanced case at LSR of 6.75.

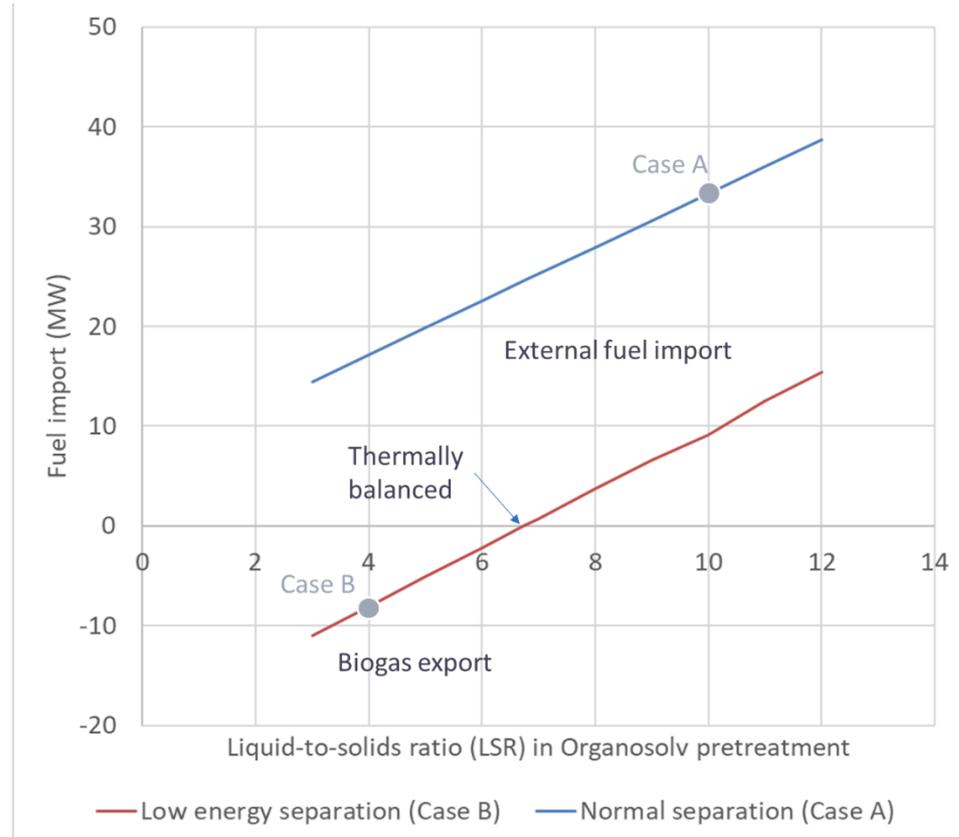


Figure 8: Fuel import (or biogas export in case of negative values) to the COS biorefinery process as a function of LSR for the base case (blue curve) and the case of energy efficient ethanol purification (red curve).

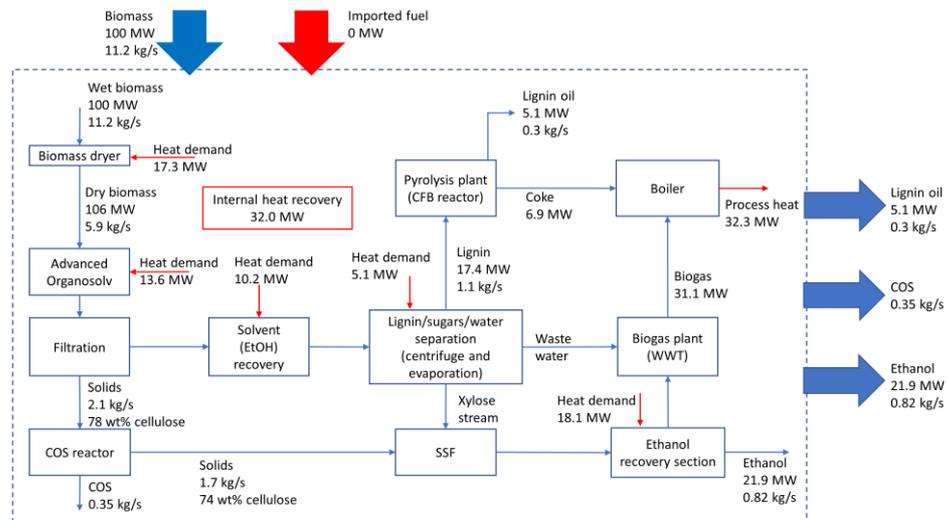


Figure 9: Mass and energy balance for the balanced COS production process (at LSR = 6.75) with low energy ethanol upgrade.

4 Results and discussion

In table 1 the major assumptions as well as the biomass input and product streams for the two cases investigated as well as for the balanced low-energy case are summarized. The production of COS, ethanol and pyrolysi oil remain unchanged between the cases as only the energy demand of different sub-processes has been changed. For case B at a very low (probably unrealistic to achieve) liquid-to-solids ratio of 4 in the advanced organosolv process, an additional export of biogas is possible increasing the thermal efficiency (accounting for thermal fuel input in relation to energy products) from 21.9 % to 35.1 %. This is mainly due to the fact that no external fuel needs to be supplied, as well as to the possibility of biogas export. Based on the sensitivity analysis on case B (with improved ethanol upgrade) the process is thermally in balance (neither import of external fuel for heat supply nor export of biogas) at a LSR of about 7 for the advanced organosolv process.

For the balanced case B the thermal efficiency in the present analysis decreases from 35.1 % (case B at LSR of 4) to 27.0 %. A higher LSR however implies a better performance of the advanced organosolv process, a parameter that has not been accounted for in the present work. This simplified analysis nevertheless gives an indication of the range of LSR that should be aimed at for commercial operation. Of course economic considerations of the value of the different by-products has to be considered to make a more relevant analysis.

Table 1: Energy efficiency for the two cases investigated, as well as for the balanced case from the sensitivity analysis.

	Case A	Case B	Case B _{balanced} ¹
<i>LSR organosolv</i>	10	4	6,75
<i>EtOH recovery energy demand</i>	high	low	low
Fuel input [MW]	133	100	100
COS [kg/s]	0.35	0.35	0.35
EtOH [MW]	21.9	21.9	21.9
Pyrolysis oil [MW]	5.1	5.1	5.1
Biogas [MW]	0	8.1	0
Thermal efficiency ²	21.9 %	35.1 %	27.0 %

¹ adjusting LSR to balance internal heat demand with internal heat generation from internal fuels

² not accounting for energy content of COS

Co-generation of electricity using a combined heat and power steam cycle (CHP), as has been accounted for by Mesfun *et al.* [2], has not been analyzed in the present study. Using some additional fuel it could be viable to generate electricity from process heat, making use of the so-called “heat pockets” in the process (see figures 5 and 7). A steam cycle could recover high temperature heat for steam generation and expansion in a turbine, supplying heat at lower temperature with back-pressure steam extraction. This could be a viable concept at commercial scale to improve the economics – partially covering internal electricity demand or even exporting (green) electricity.

The economic value of the different by-products should be carefully evaluated, even accounting for other options. Lignin is a renewable material that has been subject to a large number of different applications. The option of producing oil via pyrolysis chosen in the present study is only one among many different options. The biorefinery company Borregard in Norway for example is commercializing a process for lignin production by sulphite pulping that has a number of applications for lignin under development. Potential applications for lignin are additive use (to e.g. asphalt) or production of aromatics (still at research and development level). Cellulose is rather considered a by-product, with lignin being the main economic driver for commercialization. COS production could be one option for the cellulose-rich fraction in their proposed biorefinery framework. Ethanol production as a biofuel only process is considered not viable by industry in general, and value-added products from other side streams are a must for large scale success of these processes. ([6], [7])

Another possible modification of the current process concept could be to consider the export of biochar/-coke from the lignin pyrolysis process instead of biogas export.

References

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