

Combining expansion in pulp capacity with production of sustainable biofuels – Techno-economic and greenhouse gas emissions assessment of drop-in fuels from black liquor part-streams

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HIGHLIGHTS

- Five pathways to drop-in biofuels from black liquor part-streams are evaluated.
- Integration with energy-exporting pulp mills can reduce costs to ~80 EUR₂₀₁₇/MWh.
- Secondary feeds in black liquor gasification do not generate economic benefits.
- Hydrotreating lignin with electrolysis H₂ costs ~50% more but doubles GHG savings.
- Lignin upgrading requires industrial testing to reduce significant data uncertainty.

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ABSTRACT

Drop-in biofuels from forest by-products such as black liquor can help deliver deep reductions in transport greenhouse gas emissions by replacing fossil fuels in our vehicle fleet. Black liquor is produced at pulp mills that can increase their pulping capacity by upgrading some of it to drop-in biofuels but this is not well-studied. We evaluate the techno-economic and greenhouse gas performance of five drop-in biofuel pathways based on BL lignin separation with hydrotreatment or black liquor gasification with catalytic synthesis. We also assess how integrated biofuel production impacts different types of pulp mills and a petroleum refinery by using energy and material balances assembled from experimental data supplemented by expert input. Our results indicate that drop-in biofuels from black liquor part-streams can be produced for ~80 EUR₂₀₁₇/MWh, which puts black liquor on the same footing (or better) as comparable forest residue-based alternatives. The best pathways in both production routes have comparable costs and their principal biofuel products (petrol for black liquor gasification and diesel for lignin hydrotreatment) complement each other. All pathways surpass European Union's sustainability criteria for greenhouse gas savings from new plants. Supplementing black liquor with pyrolysis oil or electrolysis hydrogen can improve biofuel production potentials and feedstock diversity, but better economic performance does not accompany these benefits. Fossil hydrogen represents the cheaper option for lignin hydrotreatment by some margin, but greenhouse gas savings from renewable hydrogen are nearly twice as great. Research on lignin upgrading in industrial conditions is recommended for reducing the presently significant performance uncertainties.

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1. Introduction

Reducing greenhouse gas (GHG) emissions in the transport sector to a meaningful extent requires both short and long-term interventions [1]. Many interventions are built around increasing the share of renewable energy in the transport energy mix, which can be achieved by substituting fossil petrol and diesel with renewable drop-in biofuels [2]. As bio-hydrocarbons that are functionally equivalent to fossil transport fuels, drop-in biofuels are fully compatible with today's vehicle fleet and petroleum refining infrastructure [3,4]. Wider deployment of drop-in biofuels in the short-to-medium term has been identified as vital to the realization of transport GHG reduction targets [5,6].

The economics of drop-in biofuels can be enhanced by co-locating and integrating production with petroleum refineries, thereby providing valuable access to hydrogen [2,3]. The availability of cheap, ideally renewable, hydrogen is viewed as a key challenge for future development of drop-in biofuels from oxygen-rich lignocellulosic biomass feedstocks [2]. Despite growing interest, the co-processing and hydrotreatment of fossil feeds and lignocellulosic biomass-based intermediates such as pyrolysis oil and lignin in industrially representative scale remains to be fully demonstrated [7]. The lack of, and need for, representative experimental data on the hydrogen consumption and hydrocarbon product yields of different drop-in biomass-based feeds has been strongly highlighted recently [8].

As transport emission reduction targets grow in stringency, it is expected that the current feedstock base for drop-in biofuels will need broadening to meet global demand [8]. In some countries, such as Sweden, drop-in biofuels for road transport have made significant inroads in recent years, largely due to the uptake of drop-in hydrogenated vegetable oil (HVO) in the diesel pool [9]. HVO is produced predominantly from oleochemical feedstocks, such as slaughterhouse waste, used cooking oil, palm oil and palm fatty acid distillate, which are all subject to availability concerns, ranging from limited feedstock potential to contested environmental credentials [8,10]. Furthermore, drop-in biofuels for the petrol pool are commercially unavailable in meaningful quantities, which makes the timely realization of intended GHG reductions a challenging proposition [11].

Efforts are currently underway to develop drop-in biofuels from lignocellulosic forest residue-based feedstocks [12,13] as a consequence of a growing policy push for advanced biofuels [14]. One such feedstock that is viewed as an important source of renewable energy in countries with extensive forest industries is kraft black liquor (BL), which is a lignin-rich by-product of chemical pulping. Pulp mills worldwide generate more than 200 million tons of BL per year [15]. A small fraction of BL in the form of crude tall oil is already used in HVO production but the maximum potential of this fraction, amounting to only 15% of the HVO currently available on the market is very limited [16]. The most abundant component in BL, and one with significantly greater potential, is lignin, which can be upgraded to drop-in petrol and diesel blends by different pathways that can be classified into two principle production routes.

In the (*lignin*) *separation-hydrotreatment route*, around one-fifth of the lignin in the BL produced at a given mill is separated and dispatched to a petroleum refinery for hydrotreatment. Techno-economic assessments founded on knowledge from laboratory-scale tests have found the route to be profitable over a wide range of plant sizes, but refinery-integrated processes were coarsely modelled and data quality was adversely affected by low technology readiness [17,18]. Entrained-flow gasification of BL and the subsequent upgrading of syngas to biofuels constitutes the (*BL*) *gasification-catalytic synthesis route* [19]. BL can be co-gasified with similar forest residue-based feedstocks such as pyrolysis oil (PO) to increase the amount of biofuels that can be produced from the fixed quantity of BL available at an individual mill [20]. A similar capacity increase can be obtained by co-processing syngas with electrolysis hydrogen in a gasification-electricity hybrid pathway [21,22]. Whether increased yields can also translate into better economic performance has

not been investigated for the case of drop-in biofuels.

In chemical pulping, the lignin in BL is typically combusted in a recovery boiler, which can be a bottleneck to capacity expansion at some pulp and paper mills. Redirecting some of the lignin to a biofuel plant, based on either separation-hydrotreatment or gasification-catalytic synthesis, frees capacity in the recovery boiler, which can be used to increase the production of pulp, assuming no other capacity constraints are in effect. The increased pulping capacity can, in conjunction with the sale of produced biofuels, translate into significant additional revenue. It has been shown that relatively small BL gasification units, which complement rather than replace recovery boilers, may potentially also be economically competitive provided they are integrated with a pulp mill boasting a large energy surplus [18]. Such units are associated with lower technical risk and smaller investment size, two factors that have been identified as barriers to commercial deployment [23].

Upgrading lignin to drop-in biofuels will have a differential impact on the energy balance of mills that operate with a large energy surplus and mills that operate with an energy deficit. A systematic comparative investigation of how different pathways to drop-in biofuels from part-streams of black liquor perform when integrated with different types of mills has not previously been carried out, and is the principle objective of this paper.

This paper evaluates the economic and GHG performance of five biofuel pathways that can be used to produce drop-in petrol and diesel blends from part-streams of BL and thereby debottleneck pulp production capacity at recovery boiler-limited pulp mills. Two pathways belong to the separation-hydrotreatment route. These are designed to investigate enviro-economic trade-offs with direct applied relevance to the refinery industry and its energy system, such as those between the use of renewable and fossil hydrogen in refinery-integrated co-processing of fossil and biomass-based feeds. Three belong to the gasification-catalytic synthesis route. These are chosen in order to test the hypothesis that supplementing BL with secondary feedstocks such as PO and hydrogen can improve the economic case for recovery boiler debottlenecking plants.

In addition, the impact of mill energy profile on integrated energy balance and biofuel production cost, which is of interest to both policymakers and the pulp industry, is studied by examining three different pulp mill configurations with contrasting energy profiles as integration sites. The economic case for expanding pulp production capacity through a recovery boiler rebuild is not assessed, rather this paper focuses on options that can be used to combine capacity expansion with the delivery of drop-in biofuels.

2. Production routes and integration sites

2.1. Drop-in biofuel pathways

Table 1 lists the pathways evaluated in this study, classified by production route. Each pathway can be broken down into two stages. In the first stage, a part-stream of BL from the pulp mill is upgraded to an intermediate product, stabilized methanol in the gasification-catalytic synthesis route and a stabilized lignin mixture in the separation-hydrotreatment route. In the second stage, the intermediate product is upgraded to transport fuel blends at the petroleum refinery.

2.1.1. The separation-hydrotreatment route

Lignin is separated from kraft BL, purified, stabilized and sent to a petroleum refinery where it is hydrotreated to remove oxygen and upgraded to diesel and petrol blends. The lignin separation-hydrotreatment route is illustrated schematically in Fig. 1. The process configuration for the pulp mill-integrated steps is based on technology developed by Sun Carbon AB [12]. The maximum amount of lignin that can be separated from BL without adventuring recovery boiler operation is mill specific, but is typically limited to ~20%. The two pathways in this route are identical in all aspects other than the choice of hydrogen

Table 1
Key attributes of examined drop-in biofuel pathways.

Pathway	Feedstock(s)	Production Route	Product (s)
1a ^a	Lignin	Separation-Hydrotreatment	Petrol & Diesel
1b ^b	Lignin + electrolysis	Separation-Hydrotreatment	Petrol & Diesel
2a ^c	BLG	Gasification-Catalytic Synthesis	Petrol & LPG
2b ^d	BLG + electricity	Gasification-Catalytic Synthesis	Petrol & LPG
2c ^e	BLG + pyrolysis oil	Gasification-Catalytic Synthesis	Petrol & LPG

^a Lignin extracted from kraft BL by membrane separation is stabilized, purified and sent to an oil refinery for hydrotreatment and upgrading to petrol and diesel blendstock.

^b Identical to 1a except that the hydrogen used for hydrotreatment is produced by water (PEM) electrolysis.

^c Syngas from entrained-flow gasification of kraft BL is upgraded to drop-in petrol via the MTG (methanol-to-gasoline) process at a petroleum refinery.

^d Syngas from entrained-flow gasification of kraft BL is mixed with hydrogen from water (PEM) electrolysis and upgraded first to methanol and then to petrol.

^e A variant of 2a that uses blends of kraft BL and imported PO as feedstock.

supply source, namely, steam reforming of natural gas in the lignin pathway (1a) and polymer electrolyte membrane (PEM) electrolysis of water in the lignin + electrolysis pathway (1b).

A stream of weak BL from the mill evaporation unit is split by membrane separation into a lignin and hemicellulose-rich retentate stream and an alkali-rich permeate stream. The alkali compounds in the permeate are returned to the evaporator train, while the retentate is subjected to indirect steam heating, which initiates an alkali-catalyzed breakdown of the organic fraction. The hemicelluloses are subsequently also returned to the mill recovery cycle, while the depolymerized lignin fragments are acidulated with carbon dioxide, which reduces the pH and leads to the formation of a liquid lignin phase by protonation. The multiphase mixture is washed with sulfuric acid to

leach out remaining impurities. An important part of the separation-hydrotreatment route is the provision of lignin in a form that can be conveyed to the refinery and co-processed with crude oil derivatives. An organic solvent is used to generate a stable 50/50 mixture of lignin and a fossil carrier oil, namely, vacuum gas oil (VGO) with negligible alkali content that can be transported and processed at the petroleum refinery. VGO is a by-product of crude oil distillation. It is today refined into lighter hydrocarbons independently of any biofuel path.

The lignin/VGO mixture is hydrotreated in a two-step iso-cracker. In the first step, oxygen and sulfur are removed by treating the feed with hydrogen at elevated temperature and pressure in the presence of a catalyst. The bulk of the oxygen is removed by hydrodeoxygenation reactions. Partial saturation of aromatics also takes place. In the second step, the hydrocarbon products undergo cracking, isomerization and further saturation. The heavy ends are cracked into smaller components in the diesel and petrol range, which can be blended with similar fossil products.

2.1.2. The gasification-catalytic synthesis route

Pure BL or blends of BL and PO are gasified to produce syngas that, optionally combined with hydrogen from water electrolysis, is used as feedstock for the production of drop-in petrol via a methanol intermediate. A simplified process schematic of the BL gasification-catalytic synthesis route showing the process configurations of the constituent pathways is provided in Fig. 2. The gasification step common to all pathways is based on the BL gasification (BLG) technology developed by Chemrec AB [24]. For 2b and 2c, a second feedstock is used to increase biofuel production from a given volume of BL. For 2c, up to 25% PO can be mixed into the BL without any other changes to the gasification technology [25].

Concentrated BL is gasified in a pressurized refractory-lined reactor using oxygen as oxidizing and atomizing agent to produce a clean syngas made up primarily of carbon monoxide, hydrogen and carbon dioxide. Small quantities of hydrogen sulfide and methane are also present. The catalytic effect of the alkali in BL ensures nearly complete carbon conversion at relatively low reactor temperatures [26,27]. The alkaline pulping chemicals in the BL form a molten slag, which is dissolved in

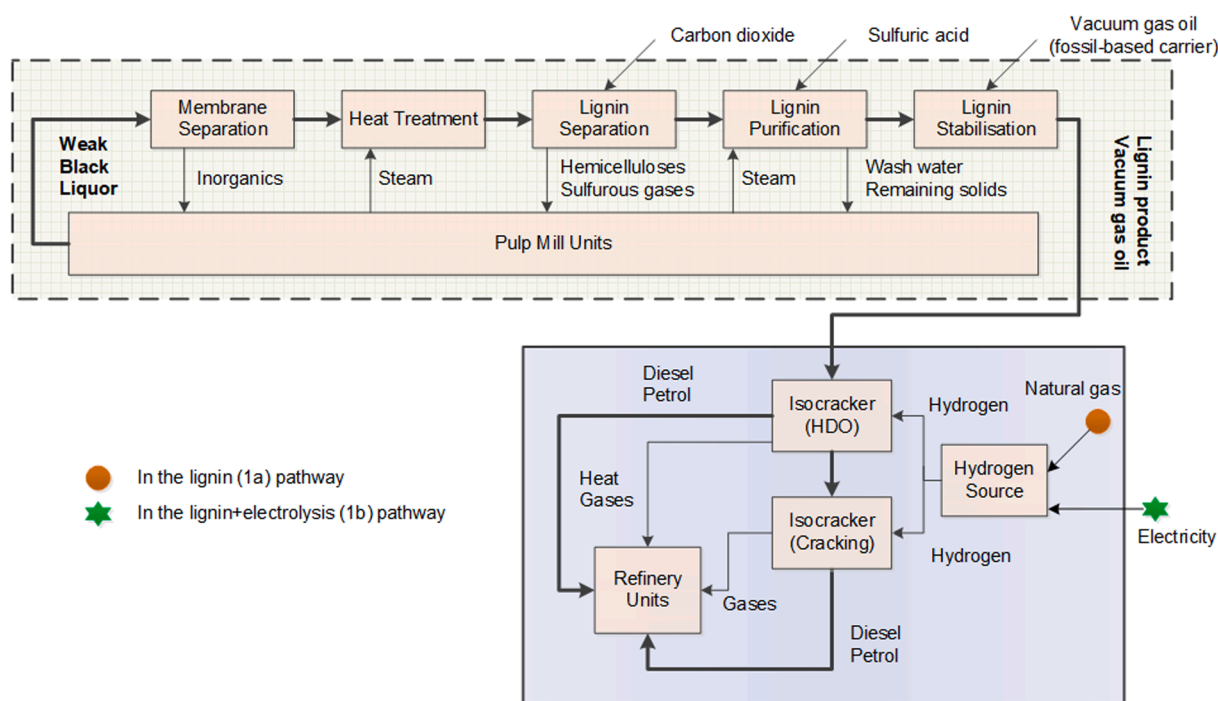


Fig. 1. Simplified process schematic for the lignin separation-hydrotreatment route. All process steps except the production of hydrogen are shared between constituent pathways 1a and 1b.

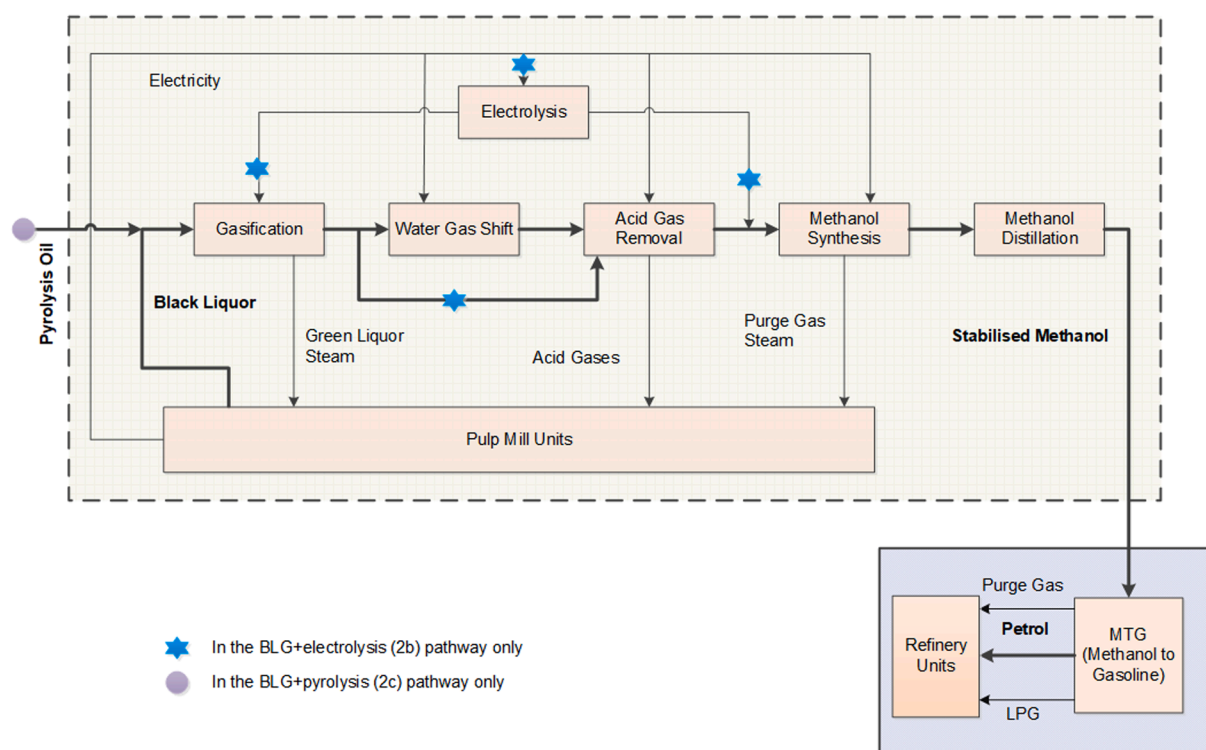


Fig. 2. Simplified process schematic for the black liquor gasification-catalytic synthesis route. There is no water gas shift in pathway 2b, syngas is sent for acid gas removal directly.

water and returned to the mill for re-use in the kraft cycle.

After leaving the reactor, syngas is cooled down to 30–40 °C in two steps. The next treatment step differs between 2a and 2c on the one hand and 2b on the other. In 2a and 2c, the composition of the cooled syngas is adjusted in a water-gas shift reactor after which carbon dioxide and hydrogen sulfide are removed by scrubbing with an amine solution. In 2b, there is no water gas shift unit. The stoichiometric requirement for methanol synthesis is satisfied by mixing syngas from the amine scrubber with hydrogen, which is produced by PEM electrolysis of water. Since amine scrubbers cannot reliably reduce the concentration of hydrogen sulfide to sub-ppm_v levels, syngas is passed through a zinc oxide bed to reduce the concentration of sulfur to below 0.1 ppm. The conditioned syngas is catalytically upgraded to crude methanol, which is partially distilled to produce water-containing “stabilized” methanol. Petrol blendstock is synthesized from stabilized methanol via the methanol-to-gasoline (MTG) process at a petroleum refinery, to take advantage of existing infrastructure [28,29]. Small quantities of LPG are also obtained as a by-product. Other gaseous by-products from the synthesis loop are combusted for energy recovery.

2.2. Kraft pulp mills

Three pulp mill configurations with different production capacities and energy requirements, as summarized in Table 2, are used as integration sites for production of biofuel intermediates. *Model Mill* is a simulation model representing a state-of-the-art market pulp mill with an energy surplus. *SKKP* (Smurfit Kappa Kraftliner Piteå) is a Swedish integrated pulp and paper mill reliant on energy import for meeting the internal demand. *Södra* (Södra Cell Mörrum) is a Swedish market pulp mill that is able to meet its own energy needs without fuel import but does not generate a noteworthy energy surplus. The evaluation in this paper represents a scenario in which a pulping capacity increase of 18.5% is obtained at each mill by directing 18.5% of the BL dry solids flow to the biofuel plant, while keeping the thermal load on the recovery boiler the same as under normal operation.

Table 2

Selected production and energy data for examined kraft mills under normal operation.

	Units	Model Mill	SKKP ^b	Södra ^d
<i>Production Data</i>				
Mill Type	–	Market Pulp	Pulp & Paper	Market Pulp
Pulp Production Capacity	tons/day	2000	1268	1288 ^c
<i>Electricity Data</i>				
Generation (Back Pressure Turbine)	MW _{el}	70	35	40
Generation (Condensing Turbine)	MW _{el}	73	–	–
Internal Consumption	MW _{el}	61	67	39
Import from Grid	MW _{el}	0	32	0
Export to Grid	MW _{el}	83	0	1
<i>Steam Data</i>				
High Pressure Steam from Recovery Boiler ^a	MW _{th}	438	192	260
High Pressure Steam from Biomass Boiler ^a	MW _{th}	66	65 ^c	1
<i>Other Data</i>				
BL to Recovery Boiler	MW _{th}	561	240	325
Feedstock to Lime Kiln	MW _{th}	34	21	22
Feedstock to Auxiliary (Biomass/Power) Boiler	MW _{th}	107	74	26–96
Process Steam Levels	MPa	1.3/1.0/0.45	2.7/1.1/0.3	2.5/1.4/1.1

^a High pressure steam levels vary between mills.

^b Based on energy data for 2017.

^c Two additional supplementary boilers supply 5 MW and 3 MW of steam at 2 and 1.6 MPa, respectively.

^d Based on energy data for September 2018.

^e Partly paper pulp, normally ~ 2/3 of the total, and partly textile pulp, normally ~ 1/3 of the total.

The Model Mill has a recovery boiler producing high pressure (HP) steam at 10.1 MPa. Falling bark is combusted in the lime kiln and the surplus can be fired in a power boiler to produce additional HP steam. The mill is equipped with a condensing turbine. The energy surplus is converted to electricity, which is exported to the grid.

The SKKP mill is furnished with two paper machines that consume large quantities of steam and electricity. The recovery boiler produces HP steam at 5.8 MPa. It is complemented by a multi-fuel biomass boiler that is fired mainly with bark from the debarking line, which produces HP steam at 12 MPa. Two additional supplementary boilers are also present. Electricity is generated by two back pressure turbines. The lime kiln is fired with a combination of sawdust, pellets and bio-oil. SKKP is a net importer of both electricity and biomass.

At the Södra mill energy for process use is supplied primarily by the recovery boiler, which produces HP steam at 5.8 MPa. The lime kiln is fired with tall oil residue. While the mill is equipped with an auxiliary biomass boiler, the steam output from the recovery boiler is normally sufficient to satisfy the process demand for steam and electricity. Although there is an excess of steam relative to the process demand, the surplus cannot be converted into electricity due to the absence of a condensing turbine and low availability in the oldest turbine (Roland Mårtensson, Personal Communication, 2020)

2.3. Petroleum refinery

The final upgrading to transport biofuels is co-located and integrated with a refinery modeled on Preem Oil Refinery, Lysekil. The Lysekil refinery has a crude oil refining capacity of 11.4 Mt per year with a gross energy demand in excess of 400 MW_{th}, which is supplied by internally produced energy gases and externally purchased natural gas. The refinery is home to a vacuum distillation unit (VDU) with a capacity of 11,000 cubic meter per day. The vacuum gas oil (VGO) from the VDU is processed in a two-step iso-cracker, which is assumed to have been rebuilt to handle biogenic feedstock such as lignin in blends with VGO. The hydrogen supplied for process use in the refinery is principally produced by steam reforming of natural gas. The product range at the Lysekil refinery includes petrol, diesel, LPG and various grades of fuel oil.

3. Methods

3.1. Study design

The biofuel plant capacity at each mill was set at 18.5% of the BL flow to the recovery boiler in the gasification pathways and the corresponding amount of lignin on an energy basis in the lignin pathways (see Table 3). The amount of energy extracted from the recovery boiler for use as input to biofuel production was therefore the same for all pathways at a given mill. However, the presence of secondary feedstocks meant that both 2b (electricity) and 2c (PO) had a higher total feedstock input than 2a, as noted in Table 3. The fraction of PO in the PO/BL blend evaluated in 2c was set at 20 wt%, as this is the highest fraction that has been verified in pilot-scale gasification experiments [30].

3.2. Process modelling

Integrated material and energy balance models were produced for each pathway using best available data supplemented by expert input. Modelling choices and assumptions for different process steps are described below, grouped by production route.

3.2.1. The separation-hydrotreatment route

The material and energy balances for the mill-integrated lignin separation and refinery-integrated hydrotreatment stages were based on data provided by SunCarbon AB and Preem AB, respectively. The weak BL fed to the membrane separation unit had a dry solids content of 22%

Table 3

Values of key process variables in the biofuel production process for each pulp mill.

	Units	Model Mill	SKKP	Södra
Recovery boiler capacity	tons dry solids BL/d	3760	2000	2700
BL to biofuel plant ^a	tons dry solids/d	695	370	500
BL to biofuel plant ^b	MW HHV dry basis	103.7	56.3	70.8
Lignin in BL to biofuel plant ^c	tons dry solids/d	348	189	238
Lignin in BL to biofuel plant ^d	MW HHV dry basis	103.7	56.3	70.8
PO to biofuel plant ^e	tons dry solids/d	160	92.7	115
PO to biofuel plant ^f	MW HHV dry basis	43.1	24.9	30.8
Hydrogen to biofuel plant	MW HHV	58.4	24.5	37.3

^a Applicable to gasification pathways (2a, 2b, 2c). Equals 18.5% of the BL input to the recovery boiler at each mill.

^b HHVs (d.b.) for BLs from Södra, SKKP and Ref Mill are 12.2 MJ/kg, 13.1 MJ/kg and 12.9 MJ/kg, respectively.

^c Application to lignin pathways (1a, 1b).

^d HHV (d.b.) for lignin is 27.8 MJ/kg [31].

^e 20/80 BL/PO blend on mass basis.

^f Based on a PO HHV (d.b.) of 23.2 MJ/kg [32].

and a lignin content of 6.5%. It was taken from the evaporator train after the removal of fatty acids and extractives. The electricity consumption of the membrane filtration unit was assumed to be negligible. Based on results from pilot-scale membrane separation experiments it was assumed that the retentate stream contained 80% of the lignin and 100% of the non-lignin organic compounds in the weak BL feed. Heat treatment of the retentate stream was carried out through indirect heat exchange with IP (intermediate pressure) steam, while LP (low pressure) steam was used in the purification and stabilization steps. Lignin was delivered to the refinery in a 50/50 lignin/VGO mixture, which was further diluted with VGO to reduce the oxygen content to 5 wt%, guided by the requirements for a commercial two-step iso-cracker.

Lignin hydrotreatment was modelled on data from lab-scale tests of a reference lignin in a 10/60/30 lignin/light light gas oil (LLGO)/renewable tall diesel (RTD) blend. Note that the reference lignin used in hydrotreatment experiments came from a different source than the lignin used for modeling the separation stage. Hydrogen consumption was calculated by subtracting the hydrogen consumption of the LLGO and RTD fractions from the total consumption of the lignin/LLGO/RTD blend. The yield structure for the hydrocracking of the heavy ends generated during lignin hydrodeoxygenation was based on VGO yield structure, as hydrocracking data for lignin was not available. The contribution of lignin to total blend yields of carbon dioxide, carbon monoxide and water was determined by subtracting the contribution from the RTD fraction. In the cases of fuel gases, petrol and diesel, lignin contribution was calculated by subtracting the contributions of both LLGO and RTD. Steam and hydrogen sulfide were assumed to originate in lignin alone. Heat release was estimated by taking the difference between the energy inputs and outputs. Potential shifts in fossil product distributions as a consequence of co-processing were ignored.

The convoluted approach outlined above reflects the present deficiency of knowledge on lignin co-processing and hydrotreatment in industrially relevant conditions (see Section 4.4 for further discussion). Results are therefore subject to large uncertainties and should be interpreted with caution.

3.2.2. The gasification-catalytic synthesis route

Energy and mass balance data for BLG was generated by thermodynamic equilibrium calculations (TECs). These were performed in SIMGAS, which is a MATLAB-based tool that uses a non-stoichiometric approach to calculate the equilibrium compositions of both the gaseous and the liquid phases [33,34]. Feedstock compositions used as

inputs to the TECs can be found in the [Supplementary Material in Appendix A](#). The gasification reactor was modelled as an oxygen-blown entrained-flow reactor pressurized at 3 MPa. The SIMGAS model solves an energy balance to calculate the amount of oxygen required to reach a reactor temperature of 1050 °C. It is known that hydrogen sulfide and methane deviate from equilibrium [33]. The former was determined by an empirical modification to the thermodynamic model. Based on past experimental studies, the latter was fixed at 1 mol% [34]. Heat loss from the reactor was set to 0.7% of the feedstock energy input.

With the exception of the zinc bed, which was assumed to be a passive component, all process steps in the production of petrol blendstock from syngas up to and including the synthesis of methanol were modeled in Aspen Plus™ 8.4. In the syngas upgrading model, saturated steam was supplied, produced, used and consumed at three pressure levels: LP steam at 0.4 MPa, MP steam at 1 MPa and IP steam at 3 MPa.

The water gas shift reactor used to raise the H₂/CO ratio in syngas to that required for methanol synthesis was modeled as an equilibrium reactor based on previous work by some of the co-authors [32]. The acid gas unit was modeled as an amine wash capable of reducing the concentration of carbon dioxide and hydrogen sulfide in syngas to 3 wt% and 10 ppm_v, respectively, using LP steam. Hydrogen was produced by PEM electrolysis of water with an electricity-to-product efficiency of 80% on a HHV basis [35]. PEM technology was selected ahead of alkali electrolysis as it is able to supply pure hydrogen at intermediate to high pressures more efficiently [36]. The oxygen produced as a by-product of electrolysis was sent to the gasifier.

Methanol synthesis was modeled as an equilibrium reactor operating at 254 °C with a temperature approach of 30 °C, an inlet pressure of 9 MPa and a pressure drop of 0.55 MPa across the methanol loop. Unconverted gas from the reactor was recycled and mixed with fresh syngas. Reactor feed was pre-heated to the required reactor inlet temperature by heat exchange with the effluent, which was cooled further with water to separate raw methanol from the mix of unconverted gases by condensation. The raw methanol was only partially distilled ("stabilized") as the MTG process appears capable of handling feeds with a purity of 96% [37]. The yield structure for MTG products was taken from a process simulation by Larson et al. [37] who, in turn, based their work on Barker et al. [38] and Schreiner [39] and found good agreement with aggregate product distributions reported by Zhao et al. [29].

3.2.3. Material and energy integration with pulp mill

In lignin separation-hydrotreatment, the inorganic constituents of the permeate stream and the hemicelluloses in the lean BL were returned to the mill evaporation unit. The sulfuric acid containing wash water stream from the lignin purification unit was sent to the mill and mixed with lean BL. The resulting increase in the amount of sulfur in the mill recovery cycle was mitigated by increasing the purge rate of electrostatic precipitator (ESP) ash from the recovery boiler. Additional sodium hydroxide was added to the recovery cycle to make up for the resulting loss of sodium that left together with the sulfur. Other points of integration included the supply of IP and LP steam at 2.5–2.8 MPa and 0.35–0.4 MPa, depending on the mill, and the combustion of sulfur-rich gases released in the lignin separation step.

In gasification-catalytic synthesis, the hydrogen sulfide separated in the amine wash was returned to the recovery boiler to avoid affecting the overall mill chemical balance. Purge gas from methanol synthesis was fired in the mill lime kiln. Electricity was imported from the mill. LP and IP steam were exported from the biofuel units to the mill, as discussed further in [Section 4.1](#).

3.2.4. Material and energy integration with petroleum refinery

All of the purge gas and 25% of the heat recovered from the MTG reactors were assumed to replace an equivalent amount of energy from natural gas. The electricity consumption of the MTG process was assumed to be negligible. The hydrogen used for the hydrotreatment of

lignin was produced at the refinery by steam reforming of natural gas in an existent reformer unit in 1a, and by PEM electrolysis with an electricity-to-product efficiency of 80% on a HHV basis in 1b. Heat and fuel gases from lignin hydrotreatment replaced the natural gas used for steam generation at the refinery in a ratio of 1:1 on an energy basis. The final upgrading of biofuel blend components was carried out at the refinery.

3.3. Energy efficiency assessment

Two different measures of efficiency were used to quantify energy performance. The system boundaries for each measure are shown in [Fig. 3](#) together with cross-boundary flows.

A system efficiency η_{system} that considers all primary energy inputs to biofuel production units is defined in Eq. (1), where $E_{\text{Primary-Inputs}}$ corresponds to the energetic value of all primary energy inputs.

$$\eta_{\text{system}} = E_{\text{Product}}/E_{\text{Primary-Inputs}} \quad (1)$$

The system boundary in Eq. (1) is drawn around the biofuel production process only, as shown in [Fig. 3](#). To account for the changes in the overall energy balance of the mill and the refinery resulting from the integration of biofuel production, an expanded system efficiency $\eta_{\text{system-exp}}$ is defined in eq. (2) where $E_{\text{Integrated-Energy-Inputs}}$ is the net energetic value of integrated energy inputs/products.

$$\eta_{\text{system-exp}} = E_{\text{Product}}/E_{\text{Integrated-Energy-Inputs}} \quad (2)$$

The primary energy inputs and integrated energy inputs/products used for efficiency calculations are listed in [Table 4](#). As per the definition of $\eta_{\text{system-exp}}$ the feedstock for both lignin and gasification pathways is not BL or BL lignin, but the net change in mill biomass and electricity balance. Similarly, in addition to biofuel products, the net change in refinery natural gas balance constitutes a secondary product. Note that the natural gas reformer supplying hydrogen in 1a is outside the expanded system boundary, while the electrolyzer used for hydrogen production in 1b is included within. The relatively small quantities of electricity and hydrogen used in the MTG process are ignored.

3.4. Economic evaluation

Economic performance was evaluated by calculating a minimum fuel selling price (MFSP) using the discounted cash flow rate of return method. The total capital investment (TCI) estimate for each pathway was in large part based on commercial nth-plant cost estimates at different levels of granularity. Cost estimates were inflation adjusted to 2017 EUR using the Plant Cost Index from Chemical Engineering Magazine and exchange rates of 9.5 SEK/EUR and 8.5 SEK/USD. Reference costs were scaled using eq. (3):

$$C_{\text{Actual}} = C_{\text{Reference}} \times (S_{\text{Actual}}/S_{\text{Reference}})^f \quad (3)$$

where C and S denote the cost and size of the component, respectively, while f denotes the scaling exponent specific to the component.

The cost composition and scaling exponents of individual process units are provided in the [Supplementary Material in Appendix B](#). Cost estimates for PEM electrolyzer systems can vary widely between studies in the literature [35,36] depending, among other factors, on how installation costs and contingency are handled [21]. The installed investment cost was set at 1500 EUR/kW_e in line with the findings of a comprehensive recent cost review [40]. The contingency for cost escalation was fixed at 30% of fixed capital investment to mitigate the risk of underestimation. To reflect arrangements likely applied in practice and to achieve better economies-of-scale, MTG units were sized to provide five times the capacity of the mill biofuel units. A similar arrangement was employed for the hydrotreatment unit in the lignin pathways, which was sized to treat 761 tons of liquefied lignin per day, thereby corresponding to 2 or 3 pulp mill equivalents, depending on the mill.

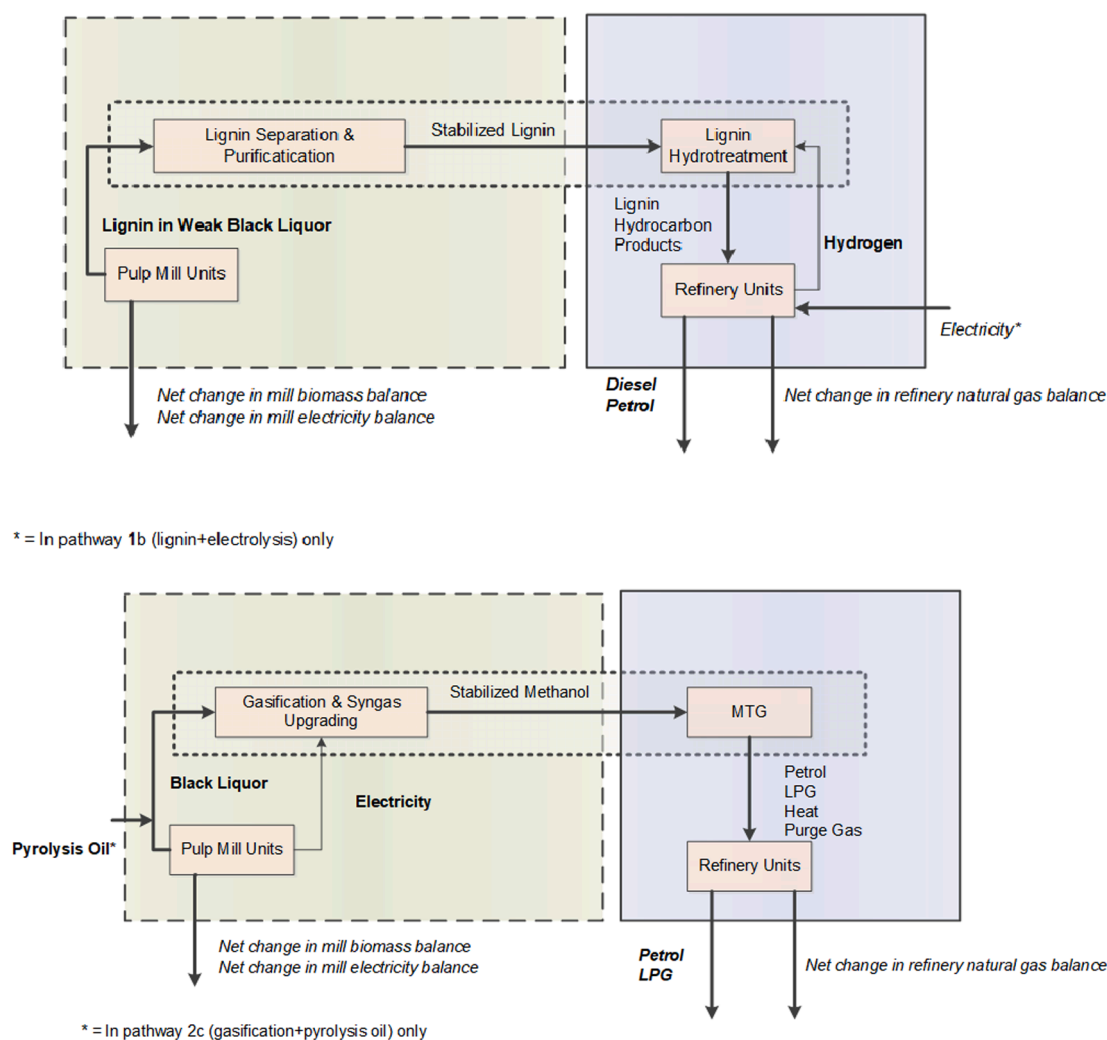


Fig. 3. Simplified schematic of system boundaries and cross-boundary flows in (i) lignin separation and hydrotreatment (top), (ii) black liquor gasification-catalytic synthesis (bottom) routes. The biofuel production process is delineated by dotted lines. The pulp mill and petroleum refinery are delineated by dashed and solid lines, respectively. Streams labelled in bold are used for calculating system efficiency. Streams labelled in italics are used to calculate expanded system efficiency.

TCI was annualized using a capital recovery factor (CRF) of 0.102, which was calculated assuming a real discount rate of 8% compounded annually over a plant lifetime of 20 years. O&M expenditure was fixed at 4% of TCI inclusive contingency. A plant availability factor of 90% was used to calculate the annual biofuel production. The prices of energy carriers and other materials that fall under operating expenditure (OPEX) are given in Table 5. Gasifier oxygen was assumed to be imported except in 2b, where the majority of the demand was met by taking oxygen from the electrolyzer. It was assumed, optimistically, that the replacement of the PEM stack due to performance degradation is carried out once over the economic lifetime of the electrolyzer. Stack replacement cost was set at 60% of installed equipment cost and included in OPEX [35].

3.5. GHG footprint assessment

GHG footprints were estimated using a simplified approach based on the Renewable Energy Directive (RED) guidelines [44]. Since RED prohibits the allocation of GHG emissions to heat even when used a co-product, such as in the case of natural gas replacement at the refinery, GHG footprints were also calculated using the principle of system expansion. The allocation of emissions on the basis of system expansion is advocated in ISO 14044 to account for the benefits associated with the replacement of fossil products and services [45]. To quantify such

benefits, an alternative estimation of GHG footprints was also carried out, which assumed that the heat released from the hydrotreatment of lignin and from the upgrading of methanol to petrol can substitute for natural gas at the refinery on a 1:1 basis. The emission factors used as inputs are listed in Table 6.

3.6. Technology maturity evaluation

The technology maturity of the examined pathways on the technology readiness level (TRL) scale was determined using two different approaches with contrasting but complementary perspectives: (a) the weighted average approach, and (b) the weakest link approach. Process configurations were broken down into smaller steps. Each step was assigned a weighting based on importance and complexity and a TRL based on the definitions provided by the European Commission [50] and the US Department of Energy [51]. In the weighted average approach, the weighted scores of all steps were added up to calculate the overall score. In the weakest link approach, the lowest score for a step with a weighting >0.2 was used as the overall score. The approaches are discussed in greater detail in a previous study [18].

Table 4
Inputs and outputs for energy efficiency calculations.

	Primary Energy Inputs [η_{system}]	Integrated Energy Inputs/ Products [$\eta_{\text{system-exp}}$]	Products [η_{system}] [$\eta_{\text{system-exp}}$]
1a	Lignin in weak black liquor ^a , hydrogen	Net change in mill biomass balance, net change in mill electricity balance, hydrogen, net change in refinery natural gas balance	Petrol, diesel
1b	Lignin in weak black liquor ^a , electricity (hydrogen)	Net change in mill biomass balance, net change in mill electricity balance, electricity (for hydrogen), net change in refinery natural gas balance	Petrol, diesel
2a	BL, electricity (utilities) ^b	Net change in mill biomass balance, net change in mill electricity balance, net change in refinery natural gas balance	Petrol, LPG
2b	BL, electricity, hydrogen ^b	Net change in mill biomass balance, net change in mill electricity balance, net change in refinery natural gas balance	Petrol, LPG
2c	BL, PO, electricity ^b	Pyrolysis oil, Net change in mill biomass balance, net change in mill electricity balance, net change in refinery natural gas balance	Petrol, LPG

^a Calculated as the difference in lignin content between weak black liquor and lignin-deficient liquor.

^b The relatively small quantities of electricity and hydrogen used in the MTG unit are ignored.

4. Results & discussion

4.1. Biofuel yields

The results from the energy balance modeling of biofuel production are summarized in Table 7. All pathways integrated with a given mill use the same quantity of BL or BL lignin, which amounts to 104 MW, 71 MW and 56 MW for Model Mill, Södra and SKKP, respectively (see Table 3 for equivalent mass flows). The differences in biofuel yields and other energy flows among the examined pathways are discussed below using Model Mill as an example. Results for other mills follow the same pattern as the conversion of feedstock to biofuel products is mill independent.

It is evident that the lignin pathways produce nearly negligible amounts of petrol with liquid hydrocarbon yields being dominated by diesel products. The total consumption of hydrogen equals 0.148 kg per kg of biofuel product, which is significantly more than the expected theoretical consumption if hydrotreatment is assumed to be limited to hydrogenolytic depolymerization and hydrodeoxygenation only. The excess can be explained by the noteworthy quantities of fuel gases that are also produced according to the experimental data used to assess the process performance. These gases were assumed to be combusted to furnish the refinery with renewable heat. As described in Section 3.2, the yield structure for lignin hydrotreatment was assembled from data embedded with large uncertainties. Experiments in industrial conditions with more representative lignin blends are planned, which may return a different product distribution. In addition, co-processing lignin with VGO can potentially also lead to a shift in the final product distribution of the latter. The nature and size of the potential shifts and their impact on refinery operation may constitute an important area for further applied research.

In contrast to the lignin separation route, the dominant product in the BL gasification route (2a, 2b, 2c) is petrol with LPG as a secondary co-product. The use of electrolysis hydrogen (2b) or a 20 wt% PO/BL blend (2c) as supplementary feedstock leads to an increase in biofuel yield by 75% and 56%, respectively.

The steam balance in Table 7 shows that the lignin separation route is

Table 5
Energy and material prices used as inputs to economic evaluations.

Bark	[EUR/MWh]	14.6	Average price for Swedish forest industry by-products in 2017
Forestry Residue	[EUR/MWh]	19.1	Average Swedish price in 2017. Transport costs are included. Excludes taxes. Woodchips from both coniferous and deciduous harvesting residues.
Electricity - Imported	[EUR/MWh]	33.5	Includes production cost, network cost and electricity tax but not VAT. Excludes the cost of electricity certificates (7 EUR/MWh).
Electricity - Exported	[EUR/MWh]	31.8	Average spot price for south-central Sweden in 2017. Does not include electricity certificate, energy tax, VAT, network cost or markup
Oxygen	[EUR/kg]	0.07	Taken from Andersson et al. [41]
Carbon dioxide	[EUR/kg]	0.10	RISE in -house estimate
Sodium Hydroxide	[EUR/kg]	0.50	RISE in -house estimate
Sulfuric Acid	[EUR/kg]	0.10	RISE in -house estimate
Solid Waste (ESP ash disposal)	[EUR/kg]	0.10	RISE in -house estimate
Additive (Lignin Product)	[EUR/kg]	6.00	SunCarbon AB in-house estimate
Zinc Oxide	[EUR/kg]	2.5	Average spot price for zinc in 2017.
Catalyst (Syngas Upgrading)	[EUR/kg methanol]	0.0011	Taken from Jafri et al. [18]
Pyrolysis Oil	[EUR/MWh]	76.0	Average of the low scenario and high scenario in "Building up the future - Cost of Biofuel" by Maniatis et al. [42]
Natural Gas	[EUR/MWh]	45.3	Average price for Swedish class I5 customers in July-December 2018. Includes the cost of natural gas, net, tax (after reduction for repayment of energy and carbon tax). Excludes general sales tax.
Hydrogen	[EUR/MWh]	54.3	Calculated as 3.564 times the price of natural gas produced using steam-methane reforming, on a mass basis. The multiple represents the average of a low and a high estimate in a previous study [18]. For steam reforming with PSA, efficiency 75–80%. IRR = 10%
Diesel Gross Margin	[EUR/MWh]	0.135	Average margin in 2016 [43]
Petrol Gross Margin	[EUR/MWh]	0.201	Average margin in 2016 [43]

Table 6
Emission factors used as inputs to GHG footprint estimations.

Input	GHG footprint [gCO ₂ eq/MJ LHV]	Comments [Source]
Forest residues	2.2	Emissions associated with "typical" technology and transport distance. 1a (lignin) and 1b (lignin + electrolysis) only [46].
Hydrogen	87.3	Emissions associated with steam methane reforming of natural gas (75 g CO ₂ eq/MJ, [47]) and natural gas supply (12.3 CO ₂ eq/MJ, estimate) 1a (lignin + electrolysis) and 2b (BLG + electrolysis) only.
Electricity	13.1	Swedish electricity mix in accordance with Swedish Energy Agency recommendation. All pathways. (Noak Westerberg, Personal Communication, 2017)
Natural gas	67.0	LCA emissions in combustion applications [48].
Petrol	93.5	Used as fossil petrol reference [49].
Diesel	95.5	Used as fossil diesel reference [49].

Table 7

Summary of energy balances for the examined pathways. Integration effects on mill and refinery energy balances are not shown. Integrated balances are detailed in the [Supplementary Material in Appendix D](#).

Pathway		Model Mill					Södra					SKKP				
		1a	1b	2a	2b	2c	1a	1b	2a	2b	2c	1a	1b	2a	2b	2c
Input																
<i>Biofuel Feedstock</i>																
Black liquor	MW _{th} HHV			104	104	104			71	71	71			56	56	56
Black liquor lignin	MW _{th} HHV	104	104				71	71				56	56			
Pyrolysis oil	MW _{th} HHV					43					31					
Electricity (Hydrogen)	MW _e				58					37					24	
<i>Others</i>																
Electricity (Process) ^a	MW _e		106	3.8	5.4	5.8		72	2.5	3.5	3.9		57	2.0	2.6	3.2
Hydrogen (Process)	MW _{th} HHV	84					58					46				
LP Steam ^b	MW _{th}	53	53				36	36				29	29			
IP Steam ^b	MW _{th}	4.4	4.4				3.0	3.0				2.4	2.4			
Outputs																
<i>Biofuel Products</i>																
Petrol	MW _{th} HHV	1.4	1.4	43	75	67	1.0	1.0	28	48	45	0.8	0.8	22	35	36
Diesel	MW _{th} HHV	84	84				58	58				46	46			
LPG	MW _{th} HHV			5.0	8.7	7.8			3.2	5.6	5.2			2.6	4.1	4.2
<i>Others</i>																
Fuel gases ^c	MW _{th} HHV	70	70				48	48				38	38			
MeOH purge ^d	MW _{th} HHV			3.6	4.1	5.3			2.3	2.7	3.6			1.9	2.1	2.9
MTG purge ^e	MW _{th} HHV			0.8	1.4	1.3			0.5	0.9	0.9			0.4	0.7	0.7
Heat ^f	MW _{th}	32	32	2.9	5.0	4.5	22	22	1.8	3.2	3.0	17	17	1.5	2.4	2.4
LP Steam ^b	MW _{th}			3.5	9.0	2.5			2.8	6.2	2.1			4.0	6.1	3.5
IP Steam ^b	MW _{th}			2.9	5.0	4.9			1.8	9.4	3.2			1.7	6.9	3.0

^a Includes electricity for hydrogen production by water electrolysis in 1b.

^b LP and IP steam are exchanged at 0.35–0.4 MPa and 2.5–2.8 MPa depending on mill. There is a small misalignment (0.05–0.2 MPa) between biofuel plant and mill steam levels, which would be fully harmonized in a physical plant.

^c From lignin hydrotreatment, used to replace natural gas at the refinery.

^d To lime kiln.

a net importer of steam from the mill. Steam is consumed during several process steps, such as heat treatment, purification and stabilization. As there are no significant temperature gradients, the potential for heat

recovery for steam generation is limited. Conversely, the biofuel production units in the BL gasification route generate a steam surplus since significant quantities of heat can be recovered during methanol

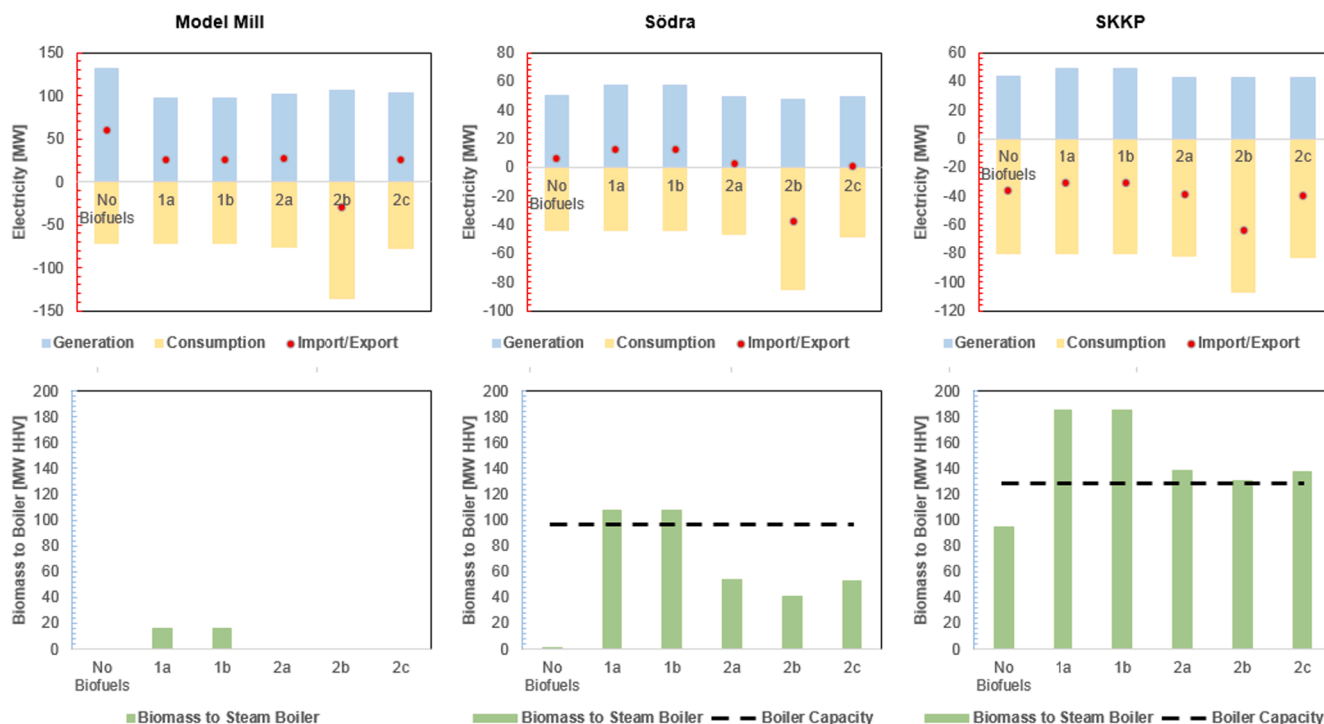


Fig. 4. Effect of biofuel production on the balance of electricity (top row) and biomass boiler (bottom row) at the studied pulp mills. See [Table 1](#) for an outline of pathways 1a-2c. Note that the y-axis scales differ among top-row plots.

synthesis and the initial cooling of syngas after the gasification reactor.

4.2. Integration impact

Results of the integrated electricity (top row) and boiler biomass (bottom row) balances under an assumed 18.5% increase in pulp production capacity are given in Fig. 4 for each mill configuration. A reference case with increased pulp capacity but no biofuels production is provided for comparison. The reference case presupposes that an increase in recovery boiler capacity of 18.5% can be realized, which is likely unrealistic at most mills. It also assumes the bark available at the Model Mill is not fired in the power boiler but is made available on the biomass commodity market.

In the reference case, the Model Mill operates with a significant electricity surplus, Södra exports only small amounts, while SKKP is a net importer of electricity. Steam from the recovery boiler can cover internal process demand at Model Mill and Södra, while additional biomass needs to be fired in the power boiler to meet the requirements of units such as the paper machines at SKKP.

The integration of biofuels leads to an increase in energy demand at the Model Mill, which is met by reducing electricity exports. In the lignin pathways, wash water from lignin purification is returned to the mill evaporator plant, leading to an increase in steam consumption. This, in conjunction with the steam requirements of various lignin processing steps, means that additional biomass is fired in the power boiler. The electricity demand of the electrolyzer in the gasification + electrolysis pathway (2b) is greater than the surplus at the Model Mill, thereby requiring the import of electricity from the grid, which affects the overall energy performance, as discussed in Section 4.3. Note that the electricity balance in Fig. 4 does not include the electricity used for producing hydrogen at the refinery in the lignin + electrolysis (1b) pathway.

Meeting electrolyzer demand in 2b requires the import of significant quantities of electricity in the case of Södra and SKKP as neither operate with an electricity surplus even without biofuel production. For Södra, the increase in steam demand in the lignin pathways is large enough that the bark-fired biomass boiler operates at the limit of its capacity (Fig. 4 bottom row, middle graph). This implies that investments in boiler capacity expansion could be required if the mill were to consider using the lignin separation route for increasing pulp production. A similar situation applies to the SKKP mill. The biomass boiler is projected to operate at or over capacity in all examined pathways (Fig. 4 bottom row, right graph). Since the lignin track is under active commercial development, there is a possibility that the specific steam consumption could come down in the near future as optimization increases with improvements in technology maturity.

BLG green liquor has a higher concentration of carbonate ions compared with recovery boiler green liquor. The specific energy requirement of the causticizing process in which carbonate is calcined is

accordingly also 40–42% greater, which translates into an additional lime kiln capacity requirement of 7.5–7.8%. The additional energy demand can be met by firing purge gas from the methanol synthesis in the lime kiln, as shown in the Supplementary Material in Figure C-1. The practicality and cost of implementing purge gas combustion at the studied mills, as well as lime kiln capacity limitations, have not been examined.

At the refinery, the energy gases and heat released during lignin hydrotreatment are used to replace natural gas, which also has a significant impact on GHG footprint, as discussed in Section 4.6. The same is true for the purge gas and heat produced as by-products in the MTG process. In addition, the need for hydrogen necessitates the import of additional natural gas in 1a and electricity in 1b.

4.3. Energy efficiencies

Energy performance results are plotted in Fig. 5. Detailed energy balances can be found in the Supplementary Material in Appendix D. System efficiencies vary between 45% and 50%, which indicates that the energy performance of lignin-based and gasification-based pathways is relatively similar when evaluated on the basis of primary energy inputs. The incremental efficiency of biofuel production from the secondary feedstocks is 61% for BLG + electrolysis (2b) and BLG + pyrolysis oil (2c), which shows that secondary feedstocks can be converted to biofuels more efficiently than pure BL when taking into account only primary inputs to the biofuel production process.

A somewhat different picture emerges when integration effects at the mill and refinery are also taken into consideration. Expanded system efficiencies are 99–256%, 51–68%, and 51–68% for Model Mill, Södra and SKKP, respectively. The efficiencies of the lignin (1a), lignin + electrolysis (1b) and BLG (2a) pathways exceed 100% when integrated with Model Mill. The main reason behind this non-intuitive result is that relatively inefficient electricity generation from BL is substituted with more efficient biofuels production. As noted above, in the expanded system the feedstock is not BL but net change in electricity and biomass. These pathways therefore offer a more energy efficient means of using the energy surplus at the Model Mill.

The lignin pathway (1a) has the highest efficiency. The only expanded energy input besides hydrogen is the reduction in the electricity surplus at the mill. In the lignin + electrolysis (1b) pathway, the electrolyzer used for the production of hydrogen is included within the system boundary and the loss of energy during conversion is visible in the energy performance. Both the lignin pathways, and to a lesser extent, the gasification pathways, benefit from the assumption that energy gases and the heat released during hydrotreatment of lignin and upgrading of methanol can substitute for fossil-derived energy at the refinery.

The BLG pathway (2a) also offers an efficient route for converting the pulp mill energy surplus into biofuels. It is a net exporter of steam to the mill and unlike pathways in the lignin separation route the only

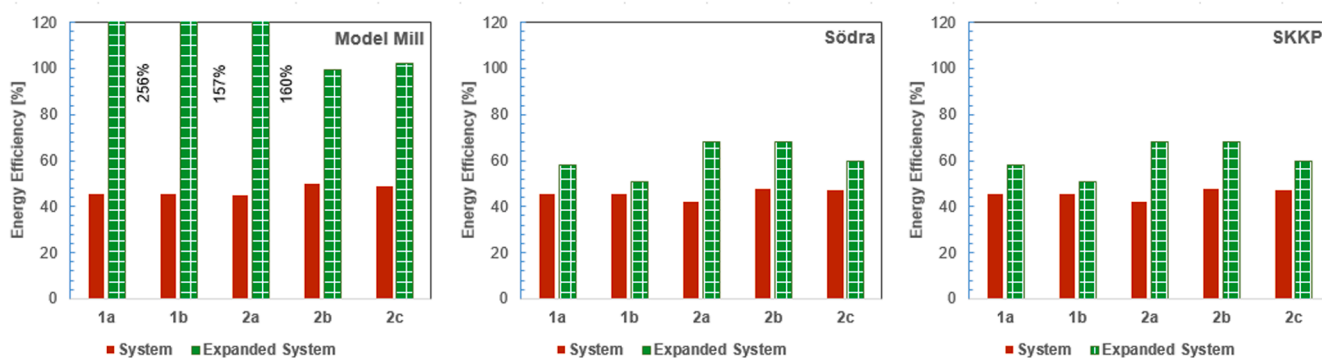


Fig. 5. System (primary energy inputs) and expanded system (overall mill and refinery balance) efficiencies for all pathways. Overshoot values are placed next to the relevant columns.

integrated input is reduction in mill electricity export. Energy losses in the process chain mean that the energy performance is similar to that of lignin + electrolysis (1b) and somewhat below that of lignin (1a). The results for BLG + electrolysis (2b) and BLG + pyrolysis oil (2c) show that using a secondary feedstock together with BL does not lead to an increase in efficiency when integration effects are taken into account.

The expanded system performance of the mills that do not benefit from an energy surplus (Södra, SKKP), is significantly lower than that of the Model Mill. An energy surplus is beneficial since the electrolysis-based pathways are large consumers of electricity, and the lignin pathways use significant quantities of steam. As noted earlier the Model Mill is able to reduce its electricity export and effectively substitute inefficiently generated electricity with more efficiently produced biofuels, while the Södra and SKKP mills need to import significant quantities of energy to meet the demand increase. The higher steam demand of the lignin pathways relative to that of the gasification pathways means that their performance degrades more significantly when integrated with mills that have a negative (SKKP) or near-zero (Södra) energy surplus.

4.4. Technology maturity

Technology readiness level scores are shown in Fig. 6. Scores and weights for individual steps in each of the studied pathways are tabulated in the [Supplementary Material in Appendix E](#).

It is clear from Fig. 6 that the TRL of the gasification-based pathways is higher than that of the lignin separation-based pathways under both the weighted average approach and the weakest link approach. All process steps in the gasification-based pathway 2a have been demonstrated in pilot scale leading to a TRL of 7 [24,29,30]. The variants with PO co-gasification (2c) and PEM electrolysis hydrogen addition (2b) have a slightly lower TRL.

The most important individual steps in the lignin separation-based pathways have TRLs of 4–6. The weakest links from a TRL perspective are the formation of a pure and stable intermediate VGO/lignin mixture from the separated lignin, and the deoxygenation and cracking of this intermediate mixture. A TRL of 4 is assigned to both these steps, corresponding to lab scale validation, but it should be noted that work is currently in progress to validate both steps in pilot scale.

4.5. Economic performance

For Model Mill with a BL feedstock input of 104 MW_{th}, the TCI estimates are 116–394 MEUR. For Södra and SKKP with BL feedstock inputs of 71 MW_{th} and 56 MW_{th}, TCI estimates are, respectively, 90–281 MEUR and 75–229 MEUR. Capital costs per MW_{th} of biofuels yield are shown in Fig. 7. The small differences in specific CAPEX between different mills are attributable to economies-of-scale. The lignin pathway (1a) has the lowest specific CAPEX, followed by BLG + pyrolysis oil (2c) and BLG (2a). With the electrolyzer unit as the dominant cost component, lignin + electrolysis (1b) has the highest specific

Specific CAPEX

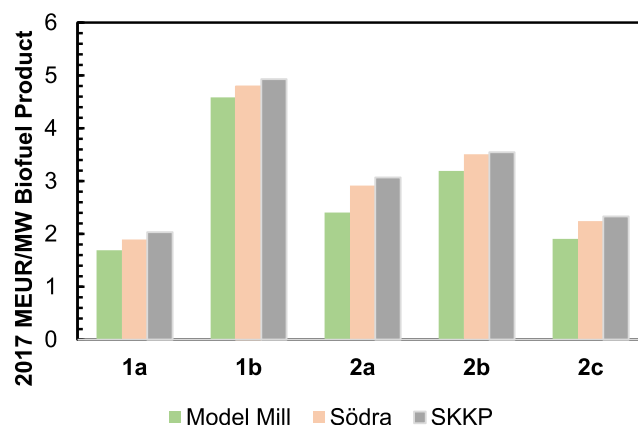


Fig. 7. Capital Expenditure per MW of biofuel product (Specific CAPEX). See Table 7 for product yields.

CAPEX, more than twice as much as that of 1a. The electrolyzer also constitutes a significant cost factor in BLG + electrolysis (2b), although the difference relative to 2a is not as large as that between the two lignin pathways. It is conceivable that projected decreases in PEM electrolysis cost as the technology grows in maturity could lower the gap further.

Biofuel production cost breakdowns and MFSPs for examined pathways are shown in Fig. 8 for each of the three mill cases. MFSPs for Model Mill range from 77 to 130 EUR/MWh. MFSPs for Södra and SKKP are between 91 and 150 EUR/MWh, and 100 and 150 EUR/MWh, respectively. The MFSPs for the best cases are better than or comparable to the reported production costs for most drop-in alternatives from similar forest residue-based feedstocks [42]. The import of biomass and electricity as a result of increased energy demand has a notably adverse impact on the economic performance of Södra and, particularly, of SKKP. The net cost of increased energy demand is significantly lower for Model Mill as a consequence of its energy surplus.

A comparison of examined pathways shows that 1a and 2a have the lowest total production costs in all mill cases. This indicates that both the gasification-catalytic synthesis route and the separation-hydrotreatment route can be used to produce biofuels from BL part-streams at comparable costs. 1b has the highest production costs, which is largely down to the high specific CAPEX of PEM electrolysis. The contrasting economic performance of the two lignin pathways (1a) and (1b) reflects the cost difference between fossil and renewable alternatives for lignin hydrotreatment. The GHG performance also differs significantly as discussed below.

The results presented in Fig. 8 appear to negate the hypothesis that the economic case for gasification-based biofuels from BL part-streams can be improved through the use of PO and hydrogen as secondary feedstocks. The specific CAPEX for 2c is lower than that for the other

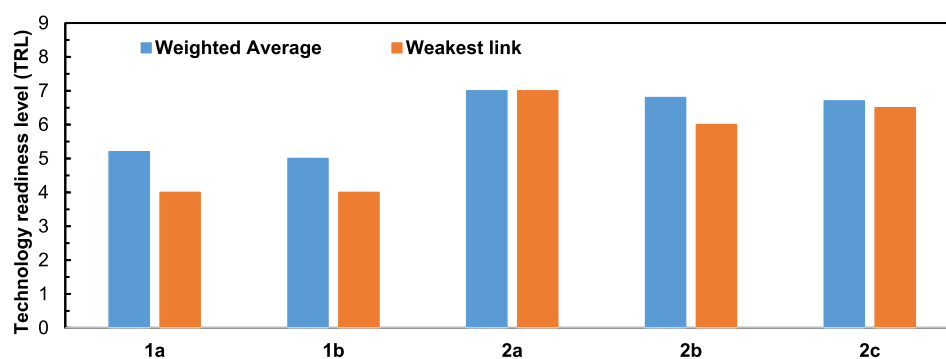


Fig. 6. Technology readiness level scores for all pathways.

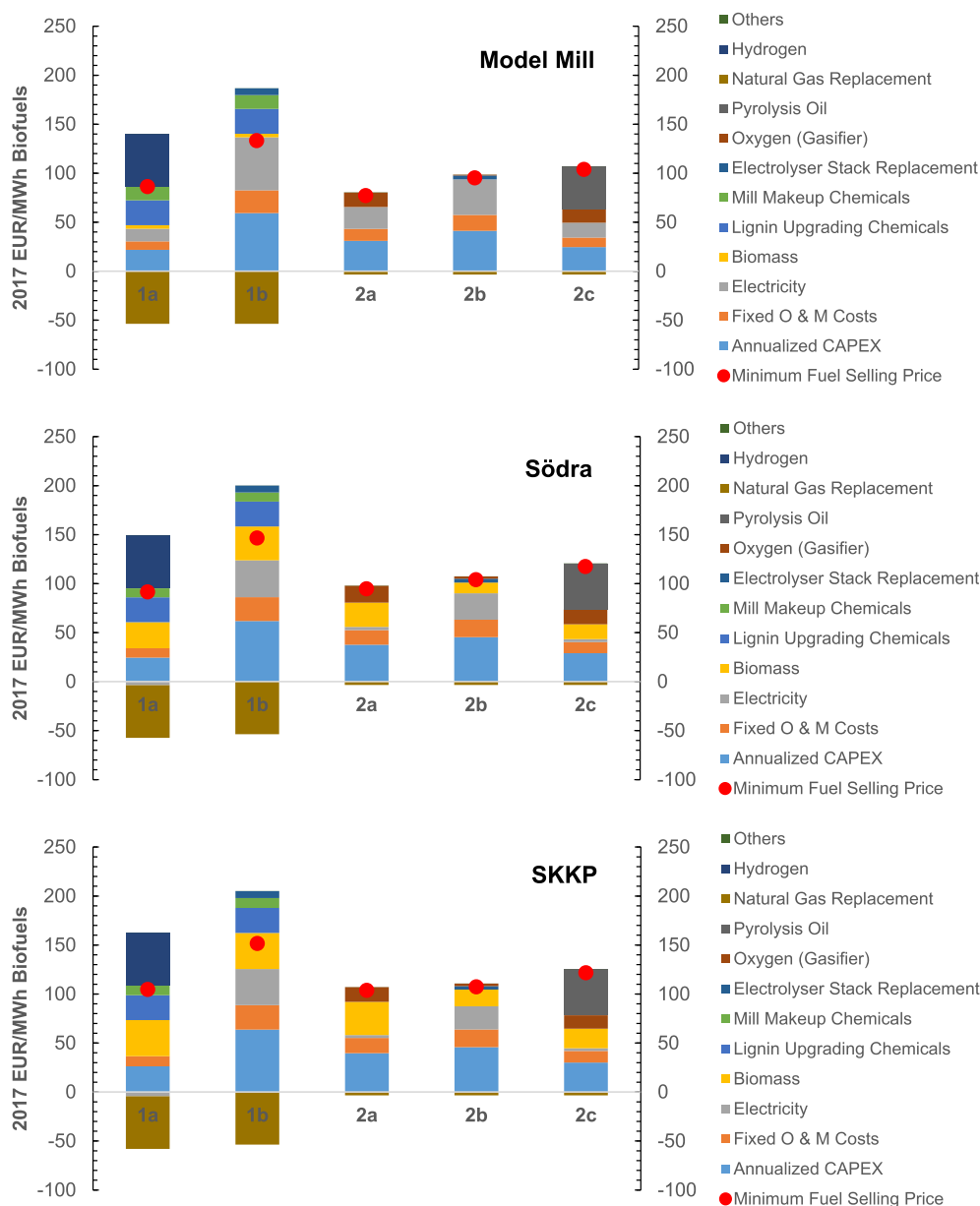


Fig. 8. Breakdown of biofuel production costs for examined pathways and mills. Lignin upgrading chemicals are carbon dioxide, sulfuric acid and stabilization additive. Mill makeup covers additional sodium hydroxide and ESP ash disposal costs. The savings from the replacement of natural gas with energy gases are included as a negative cost. Costs associated with methanol synthesis catalyst renewable, zinc oxide replacement and fossil production are aggregated under the label “Others”.

gasification-based alternatives but the costs associated with the purchase of PO, which is priced at 76 EUR/MWh, exceed the economic gain from increased biofuel yields. The economic viability of 2c is therefore dependent to a significant extent on the market price of PO. Similarly, the economic performance of 2b is markedly influenced by electrolyzer investment cost with the cost difference compared to BLG (2a) being 4–18 EUR/MWh. A reduction in electrolysis cost by a third could put 2b on an equal footing with the best performing alternatives (1a, 2a).

4.6. GHG footprints

A simplified approach grounded in the RED method for emission allocation has been used to estimate GHG footprints. Results are given in Fig. 9 (left), which also displays estimates compiled using an alternative approach based on system expansion (right). Under the RED method, GHG emissions for the examined pathways range between 29 gCO₂/MJ LHV for lignin (1a) and –33 gCO₂/MJ LHV for lignin + electrolysis

(1b), with the gasification pathways falling in the middle. These numbers translate into GHG emission savings of 69–135% compared to fossil-based petrol and diesel references of 93.5 and 95.5 gCO₂/MJ LHV, respectively.

It is evident from the results that the fossil hydrogen used for lignin hydrotreatment in 1a is by far the largest source of GHG emissions across all pathways. The recently adopted RED II requires new-built plants to deliver GHG savings of 65%. Without the significant mitigating effect of the energy gases replacing natural gas at the refinery, 1a falls short of the savings requirement. Energy gases are a product of lignin hydrotreatment, which has a highly uncertain yield structure based on current knowledge, as discussed previously. A shift in the product distribution towards petrol at the expense of energy gases could put 1a at the risk of failing to meet the RED II target, particularly if the hydrogen consumption remains unchanged. However, better experimental data is needed before a more definitive assessment can be attempted.

It can be seen from Fig. 9 (right) that the GHG footprint for 1a is

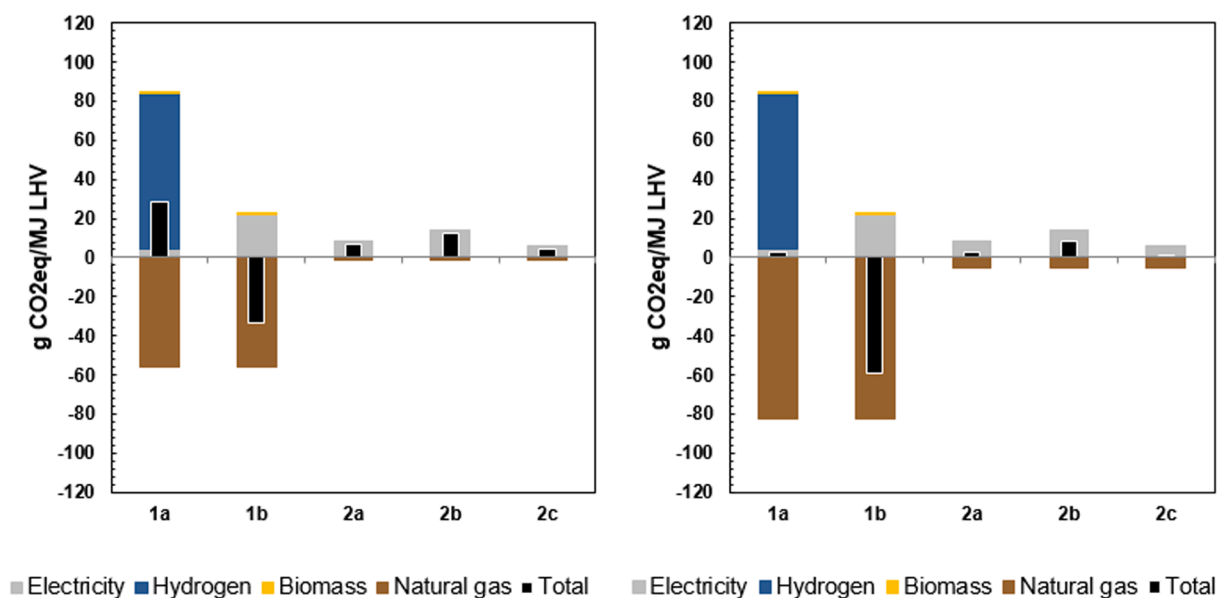


Fig. 9. GHG footprint estimates for examined biofuel pathways derived using RED methodology (left) and an alternative approach based on system expansion (right). A Swedish electricity mix is assumed. Results shown are for Model Mill.

significantly smaller when emissions are estimated using the principle of system expansion, which permits the crediting of emission savings associated with the replacement of natural gas with heat from lignin hydrotreatment. A comparison of 1a with 1b, which has net negative GHG emissions clearly demonstrates the extent of the reduction that can be achieved by switching to electrolysis hydrogen. Finally, all of the gasification-based pathways are able to satisfy the savings requirements in RED II as the expanded system feedstocks, biomass and Swedish electricity, both have low GHG footprints.

5. Conclusions

Five pathways for upgrading part-streams of black liquor to drop-in biofuels, which also permit the debottlenecking of pulp production at recovery boiler-limited pulp mills are techno-economically evaluated to establish their energetic, economic and greenhouse gas emission performance, and to identify attendant trade-offs.

The results of the economic evaluation show that black liquor part-streams can be used to produce drop-in biofuels with production costs of ~ 80 EUR₂₀₁₇/MWh, thereby equaling or bettering the economic performance of comparable forest residue-based feedstocks. The best performing pathways in the (lignin) separation-hydrotreatment and (black liquor) gasification-catalytic synthesis routes were found to have broadly similar production costs. Both routes are therefore potentially attractive options for recovery boiler-limited pulp mills looking to increase pulp capacity and broaden product portfolios through comparatively modest investments. The gasification-catalytic synthesis route has a higher technology readiness level on average, but the gap is expected to shrink notably in the near future as key process steps in the separation-hydrotreatment route undergo planned demonstration in industrial conditions. However, our lignin upgrading results are subject to large uncertainties, being based on lab testing of a reference lignin in the absence of representative industrial data.

The use of natural gas as hydrogen source represents the cheaper option (1a) for lignin hydrotreatment by some margin, but is accompanied by greenhouse gas savings that are smaller relative to those from other pathways. This can be disadvantageous under certain policy support instruments, such as the current Swedish quota obligation scheme for drop-in biofuels, which are designed to reward biofuels with high greenhouse gas emission reductions. At the same time, the large capital cost of proton exchange membrane electrolyzers makes it unlikely that

the renewable-hydrogen pathway (1b) will be economically competitive in the near future. The use of alkaline electrolyzers represents a potential option for cost reduction that has not been investigated in this study. Future availability of cheaper electrolyzers and reliable experimental data on lignin hydrotreatment are likely to impact the trade-off between fossil and renewable hydrogen in the medium term.

The hypothesis that secondary feedstocks such as hydrogen (2b) and pyrolysis oil (2c) can improve the economic performance of small-scale debottlenecking units based on black liquor gasification (2a) has not been proven. However, results in this question are sensitive to future developments in the price of pyrolysis oil and the capital cost of electrolyzers.

Electrolyzers are large consumers of electricity, and lignin separation uses significant quantities of steam. Mills operating with an energy surplus exported as electricity therefore have a significant advantage as integration sites. Mills that operate their biomass or power boilers at or near capacity may have to invest in extra capacity to meet the increased demand from biofuel integration. For a pulp mill looking to expand pulping capacity through the production of drop-in biofuels from black liquor, integration aspects that require more detailed investigation include the impact on evaporator loads, relevant for lignin pathways, and lime kilns, pertinent for gasification pathways.

Since the demand for forest residue-based drop-in alternatives that can replace both petrol and diesel is expected to grow globally, the complementary deployment of black liquor gasification-catalytic synthesis and lignin separation-hydrotreatment can be a strategically interesting option for achieving deep reductions in transport greenhouse gas emissions.

CRedit authorship contribution statement

Jafri Yawer: Methodology, Investigation, Data curation, Visualization, Writing - original draft, Writing - review & editing. **Wetterlund Elisabeth:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration, Funding acquisition. **Mesfun Sennai:** Investigation, Resources, Data curation. **Rådberg Henrik:** Validation, Investigation, Resources. **Mossberg Johanna:** Writing - review & editing, Supervision. **Hulteberg Christian:** Validation, Resources. **Furusjö Erik:** Conceptualization, Methodology, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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References

- Masson-Delmotte V, Zhai P, Pörtner H-O, Roberts D, Skea J, Shukla PR, et al. IPCC, 2018: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of cli; 2019.
- Dyk S van, Su J, McMillan JD, Saddler J (John) N. "Drop-In" Biofuels: The key role that co-processing will play in its production; 2019.
- Karatzos S, Dyk JS Van, Task IEAB, Biotechnology FP. Drop-in biofuel production via conventional (lipid/fatty acid) and advanced (biomass) routes. Part I; 2017. <https://doi.org/10.1002/bbb>.
- Palankov TA, Dementiev KI, Khadzhiev SN. Promising processes for producing drop-in biofuels and petrochemicals from renewable feedstock (Review). *Pet Chem* 2019;59:438–46. <https://doi.org/10.1134/S096554411904011X>.
- Singh R, Kalligeros S, Uppal J. Advance Biofuels in India: A comparative analysis between India and the EU for cooperation and investment; 2018.
- Taptich M, Scown C, Piscopo K, Horvath A. Drop-in biofuels offer strategies for meeting California's 2030 climate mandate. *Environ Res Lett* 2018; 13. <https://doi.org/10.1088/1748-9326/aadcb2>.
- Brown A, Waldheim L, Landälv I, Saddler J, Ebadian M, McMillan JD, et al. Advanced biofuels – potential for cost reduction; 2020.
- van Dyk S, Su J, Mcmillan JD, Saddler J (John). Potential synergies of drop-in biofuel production with further co-processing at oil refineries. *Biofuels, Bioprod Biorefining* 2019; 13: 760–75. <https://doi.org/10.1002/bbb.1974>.
- Energimyndigheten. Drivmedel 2018 Redovisning av rapporterade uppgifter enligt drivmedelslagen, hållbarhetslagen och reduktionsplikten. Bromma; 2019.
- Energimyndigheten. Kontrollstation 2019 för reduktionsplikten Reduktionsplikten utveckling 2021–2030; 2019.
- Energimyndigheten. Komplettering till Kontrollstation 2019 för reduktionsplikten. vol. 1. 2019.
- SunCarbon. Technology. www.suncarbon.se/en/technology/ [accessed April 19, 2020].
- Shell. Integrated Hydrolysis and Hydroconversion. [https://www.shell.com/business-customers/catalysts-technologies/licensed-technologies/benefits-of-biofuels/ih2-technology/hydrolysis.html#iframe=L2h5ZHVjcHlyb2x5c2ZlLWZvcml0](http://www.shell.com/business-customers/catalysts-technologies/licensed-technologies/benefits-of-biofuels/ih2-technology/hydrolysis.html#iframe=L2h5ZHVjcHlyb2x5c2ZlLWZvcml0) (accessed September 10, 2020).
- Chiaromonte D, Goumas T. Impacts on industrial-scale market deployment of advanced biofuels and recycled carbon fuels from the EU Renewable Energy Directive II. *Appl Energy* 2019;251:113351. <https://doi.org/10.1016/j.apenergy.2019.113351>.
- Abdulkhani A, Amiri E, Sharifzadeh A, Hedjazi S, Alizadeh P. Concurrent production of sodium lignosulfonate and ethanol from bagasse spent liquor. *J Environ Manage* 2019;231:819–24. <https://doi.org/10.1016/j.jenvman.2018.10.032>.
- Grahn M, Hansson J. Prospects for domestic biofuels for transport in Sweden 2030 based on current production and future plans. *Wiley Interdiscip Rev Energy Environ* 2015;4:290–306. <https://doi.org/10.1002/wene.138>.
- Anheden M, Kulander I, Pettersson K, Wallinder J, Vamling L, Hjerpe CJ, et al. Determination of potential improvements in bio-oil production (ImproOil). Gothenburg, Sweden: Report No 2017:16, f3 - The Swedish Knowledge Centre for Renewable Transport Fuels; 2017.
- Jafri Y, Wetterlund E, Anheden M, Kulander I, Håkansson Å, Furujsjö E. Multi-aspect evaluation of integrated forest-based biofuel production pathways: Part 2. Economics, GHG emissions, technology maturity and production potentials. *Energy* 2019;172:1312–28.
- Jafri Y. Entrained-flow gasification of black liquor and pyrolysis oil: experimental and equilibrium modelling studies of catalytic co-gasification. Luleå University of Technology; 2016.
- Andersson J, Furujsjö E, Wetterlund E, Lundgren J, Landälv I. Co-gasification of black liquor and pyrolysis oil: Evaluation of blend ratios and methanol production capacities. *Energy Convers Manage* 2016;110:240–8. <https://doi.org/10.1016/j.enconman.2015.12.027>.
- Brynolf S, Taljegard M, Grahn M, Hansson J. Electrofuels for the transport sector: A review of production costs. *Renew Sustain Energy Rev* 2018;81:1887–905. <https://doi.org/10.1016/j.rser.2017.05.288>.
- Hannula I. Hydrogen enhancement potential of synthetic biofuels manufacture in the European context: A techno-economic assessment. *Energy* 2016;104:199–212. <https://doi.org/10.1016/j.energy.2016.03.119>.
- Bauer F, Coenen L, Hansen T, McCormick K, Palgan YV. Technological innovation systems for biorefineries: a review of the literature. *Biofuels, Bioprod Biorefining* 2017;11:534–48. <https://doi.org/10.1002/bbb.1767>.
- Landälv I, Gebart R, Marke B, Granberg F, Furujsjö E, Löwnertz P, et al. Two years experience of the BioDME Project - A Complete Wood to Wheel Concept. *Environ Prog Sustain Energy* 2014;33:744–50.
- Furujsjö E, Pettersson E. Mixing of fast pyrolysis oil and black liquor: preparing an improved gasification feedstock. *Energy Fuels* 2016;30:10575–82. <https://doi.org/10.1021/acs.energyfuels.6b02383>.
- Bach-oller A, Kirtania K, Furujsjö E, Umeki K. Co-gasification of black liquor and pyrolysis oil at high temperature : Part 2. Fuel conversion. *Fuel* 2017;197:240–7. <https://doi.org/10.1016/j.fuel.2017.01.108>.
- Umeki K, Häggström G, Bach-Oller A, Kirtania K, Furujsjö E. Reduction of tar and soot formation from entrained-flow gasification of woody biomass by alkali impregnation. *Energy Fuels* 2017;31:5104–10. <https://doi.org/10.1021/acs.energyfuels.6b03480>.
- Yurchak S. Development of Mobil's Fixed-Bed Methanol-to-Gasoline (MTG) Process. In: Bibby DM, Chang CD, Howe RF, Yurchak SBT-S in SS and C, editors. *Methane Convers.*, vol. 36, Elsevier; 1988, p. 251–72. [https://doi.org/https://doi.org/10.1016/S0167-2991\(09\)60521-8](https://doi.org/https://doi.org/10.1016/S0167-2991(09)60521-8).
- Zhao X, McGihon RD, Tabak SA. Coal to clean gasoline. *Hydrocarb Eng* 2008; 13: 39–49.
- Jafri Y, Furujsjö E, Kirtania K, Gebart R, Granberg F. A study of black liquor and pyrolysis oil co-gasification in pilot scale. *Biomass Convers Biorefinery* 2017;8: 1–12. <https://doi.org/10.1007/s13399-016-0235-5>.
- Tikka P. Papermaking science and technology: chemical pulping. Part 2: Recovery of Chemicals and Energy. 6. Paperi ja Puu Oy; 2008.
- Carvalho L, Lundgren J, Wetterlund E, Wolf J, Furujsjö E. Methanol production via black liquor co-gasification with expanded raw material base – Techno-economic assessment. *Appl Energy* 2018;225:570–84. <https://doi.org/10.1016/j.apenergy.2018.04.052>.
- Carlsson P, Marklund M, Furujsjö E, Wiinikka H, Gebart R. Experiments and mathematical models of black liquor gasification – influence of minor gas components on temperature, gas composition, and fixed carbon conversion. *TAPPI J* 2010;9:15–24.
- Furujsjö E, Jafri Y. Thermodynamic equilibrium analysis of entrained flow gasification of spent pulping liquors. *Biomass Convers Biorefinery* 2016;8:1–13. <https://doi.org/10.1007/s13399-016-0225-7>.
- Bertuccioli L, Chan A, Hart D, Lehner F, Madden B, Eleanor Standen. Fuel cells and hydrogen Joint undertaking Development of Water Electrolysis in the European Union; 2014.
- Schmidt O, Gambhir A, Staffell I, Hawkes A, Nelson J, Few S. ScienceDirect Future cost and performance of water electrolysis: An expert elicitation study. *Int J Hydrogen Energy* 2017;42:30470–92. <https://doi.org/10.1016/j.ijhydene.2017.10.045>.
- Larson E, Williams R, Kreutz T, Hannula I, Lanzini A, Liu G. Energy, environmental, and economic analyses of design concepts for the co-production of fuels and chemicals with electricity via co-gasification of coal and biomass. United States; 2012. <https://doi.org/10.2172/1047698>.
- Barker E, Begovich JM, Clinton JH, Johnson PJ. Aspen modeling of the tri-state indirect liquefaction process; 1983.
- Schreiner M. Research guidance studies to assess gasoline from coal by methanol-to-gasoline and sasol-type Fischer-Tropsch technologies. Final report. United States; 1978. <https://doi.org/10.2172/6348367>.
- Glenk G, Reichelstein S. Economics of converting renewable power to hydrogen. *Nat Energy* 2019;4:216–22. <https://doi.org/10.1038/s41560-019-0326-1>.
- Andersson J, Lundgren J, Furujsjö E, Landälv I. Co-gasification of pyrolysis oil and black liquor for methanol production. *Fuel* 2015;158:451–9. <https://doi.org/10.1016/j.fuel.2015.05.044>.
- Maniatis K, Waldheim L, Kalligeros S. Building up the future cost of biofuel sub group on advanced biofuels; 2017.
- Energimyndigheten. 2016-012009: Övervakningsrapport avseende skattebefrielse för flytande biodrivmedel under 2016. Eskilstuna, Sweden: Energimyndigheten; 2017.
- Commission E. Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of

- petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amend. vol. L 140; 2009.
- [45] ISO. ISO 14044:2006; 2006.
- [46] Gode J, Martinsson F, Hagberg L, Palm D. Miljöfaktaboken 2011 Uppskattade emissionsfaktorer för bränslen, el, värme och transporter. Stockholm: Värmeförsk Service AB; 2011.
- [47] Sun P, Young B, Elgowainy A, Lu Z, Wang M, Morelli B, et al. Criteria air pollutants and greenhouse gas emissions from hydrogen production in U.S. steam methane reforming facilities. *Environ. Sci. Technol.* 2019;53:7103–13. <https://doi.org/10.1021/acs.est.8b06197>.
- [48] Koffi B, Cerutti AK, Duerr M, Iancu A, Kona A, Janssens-Maenhout G. Covenant of mayors for climate and energy: default emission factors for local emission inventories Version 2017. Luxembourg; 2017. <https://doi.org/10.2760/290197>.
- [49] European Commission. Proposal for a Directive of the European Parliament and of the Council on the promotion of the use of energy from renewable sources (recast) 2016;COM; 2016.
- [50] European Commission. Technology readiness levels (TRL). *Horiz 2020 – Work Program 2014-2015*; 2014. https://ec.europa.eu/research/participants/data/ref/h2020/wp/2014_2015/annexes/h2020-wp1415-annex-g-trl_en.pdf [accessed May 24, 2018].
- [51] US DOE. 2014 Technology readiness assessment; 2015. <https://doi.org/10.1080/08956308.2010.11657640>.