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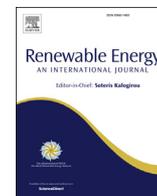
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Techno-economic evaluation of a biorefinery to produce γ -valerolactone (GVL), 2-methyltetrahydrofuran (2-MTHF) and 5-hydroxymethylfurfural (5-HMF) from spruce

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ABSTRACT

In this study, a biorefinery concept is presented to produce valuable platform chemicals such as γ -valerolactone (GVL), 2-methyltetrahydrofuran (2-MTHF) and 5-hydroxymethylfurfural (5-HMF) from lignocellulosic biomass via aqueous phase processing. Process simulation models are developed using Aspen Plus and a techno-economic assessment including cost estimation, energy integration, profitability study, sensitivity analysis and Monte Carlo simulation-based uncertainty analysis is carried out for evaluating the economic potential of the proposed process. The total investment for a plant with an annual production capacity of 35 kt of GVL, 17 kt of 2-MTHF and 5 kt of 5-HMF, is estimated as 257 M€. The minimum selling prices (MSPs) of GVL, 2-MTHF and 5-HMF are estimated to be 1.91 €/kg, 1.64 €/kg, and 1.93 €/kg, respectively. The profitability study revealed that the process generates an internal rate of return of 15.90%, making it viable and profitable. The sensitivity analysis indicated that the annual operational costs and fixed capital investment have the biggest influence on the minimum selling price of the products. Furthermore, based on the uncertainty analysis, the probability of loss is estimated as 17%. According to the market potential assessment, the most promising application of these platform chemicals is as biofuels and solvents.

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1. Introduction

In today's scenario, chemicals are produced mainly from non-renewable feedstocks such as coal, natural gas, and petroleum. The diminishing trend in the availability of these fossil fuels coupled with their harmful impact on the environment has led to the need for more research to find alternative sources which are not only renewable but also sustainable. As such, lignocellulosic biomass is one such resource that is renewable and abundantly available and has been further identified and demonstrated as a sustainable resource to produce biofuels, platform chemicals, and their respective value-added products [1,2]. Renewable energy resources are projected to play a significant part in future attempts to reduce carbon emissions and improve the global energy supply. Biofuels produced from renewable sources such as lignocellulosic biomass have the potential to be one of the biggest sources of clean, renewable, and sustainable energy, especially for transportation

and power generation [3,4].

Lignocellulosic biomass is mainly consisting of cellulose (30–50 wt%), hemicellulose (20–30 wt%), and lignin (10–30 wt%) [5]. The development of economical and technically feasible strategies for the conversion lignocellulosic biomass to value-added chemicals and fuels remains a significant challenge due to the structural difference between the biomass components. For instance, cellulose contains anhydrous glucose units and hemicellulose consists of different C5 sugar monomers. On the other hand, lignin is a complex, three-dimensional, and cross-linked biopolymer having phenylpropane units with relatively hydrophobic and aromatic properties [6,7]. As a result, different upgrading techniques [8] and energy efficient processes need to be developed to ensure optimal utilization of the biomass components.

Bio-based chemicals can help replace a large fraction of industrial chemicals and materials produced from fossil resources. The two main components of biomass, cellulose and hemicellulose can be upgraded into valuable platform chemicals such as GVL, 2-MTHF and 5-HMF, thereby enabling additional revenue generation from biomass. GVL is a colorless liquid with a sweet and herbaceous odor,

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making it suitable for use in the production of food additives. The cyclic carboxylic ester is both stable and reactive enough to be used in biofuel or solvent applications [9,10]. 5-HMF is a light yellow, crystalline chemical with a low melting point [11]. It has promise to be a high-value, bio-based platform chemical, with use in a wide range of applications, including solvents, biofuels, adhesives and polymers [12]. 2-MTHF is a colorless liquid with an ether-like odor, which has low miscibility with water and excellent stability compared to solvents, such as tetrahydrofuran (THF). These properties make it suitable for use in organometallic syntheses and as a promising green solvent, which could replace THF [13].

In literature, several commercial scale biomass conversion technologies have been proposed. For instance, the Biofine process [14] converts lignocellulosic biomass into platform chemicals such as levulinic acid by acid hydrolysis. The primary drawback of this approach is the inefficiency with which it separates and recovers levulinic acid from dilute aqueous solutions. Furthermore, the energy needs, and water requirements are very high in comparison to other methods [15,16]. Another thing to emphasise about the Biofine Process is that it is cumbersome to operate since the first reactor frequently clogs [17].

The integrated approach reported in the article seeks to promote the field of renewable energy through efficient utilization of biomass and its components (lignin, cellulose and hemicellulose) for the development of a sustainable and circular bioeconomy. The process scheme reported is energy-efficient and produces multiple valuable platform chemicals such as GVL, 2-MTHF and 5-HMF, which find main application as biofuels or biofuel additives and can be sold at a competitive market price, thereby making the integrated process profitable and adding value to income generation in biorefineries.

2. Methods

2.1. Process design basis and assumptions

The integrated process concept presented in this study relies on thermochemical conversion of lignocellulosic biomass and is a combination of different processing steps such as biomass fractionation into its constituent cellulose and hemicellulose sugars by steam pre-treatment in the presence of an acid catalyst (SO₂), upgrading of sugars into platform chemicals through the formation of intermediates and utilization of the lignin and humins obtained

during the process for energy generation in order to satisfy the heating demand of the process. GVL is one of the main products produced in the reported biorefinery approach and the production strategy selected minimizes the operational expenses and gives maximum GVL yield, through the intermediate production of levulinic acid, which has close to 100% conversion. The main advantages of the process layout presented in this study include (i) complete utilization of biomass components to make the biorefinery self-sustaining in terms of energy demand needed, (ii) Low water requirements and high recovery of solvents such as THF (iii) steam explosion as a pre-treatment method is quite efficient and has low environmental considerations.

The feasibility of the process is evaluated by carrying out a techno-economic analysis that includes conceptual process design, rigorous mass and energy balances using commercial simulation tools such as Aspen Plus, investment and operational cost estimation, profitability assessment, sensitivity analysis to evaluate the impact of key economic parameters and uncertainty analysis using monte-carlo simulations to determine the probability of risk. Table 1 lists the main economic parameters and assumptions employed in this study. The prices of the raw-materials, utilities and catalysts employed in this study are shown in Table 2.

The fixed capital investment (FCI) is calculated as the sum of inside battery limit (ISBL) costs, outside battery limit (OSBL) costs, indirect costs, contingency cost, and the initial catalyst cost. The ISBL, OSBL and indirect costs are estimated as a fraction of the delivered equipment cost (DEC) using factors from Peters et al. [20] by considering a solid-fluid processing plant, as shown in Table 3. The delivered equipment cost is calculated using Eq. (1) by considering a delivery allowance of 10%. The ISBL accounts for costs related to the purchase of equipment, equipment installation, instrumentation and controls, piping, electrical systems and the OSBL includes costs related to buildings, yard improvements and service facilities. The costs related to engineering & supervision, construction, legal expenses, and contractor's fee are accounted for in the indirect costs. The total investment is calculated as the sum of fixed capital investment, working capital and start-up capital.

$$\text{Delivered equipment cost (DEC)} = 1.1 \times \text{purchased equipment cost (PEC)} \quad (1)$$

The annual operating cost is calculated as the sum of variable operating expenses (VOE), fixed operating expenses (FOE) and

Table 1
Assumptions employed in techno-economic analysis.

| Evaluation year | 2020 |
|---------------------------------|---|
| Plant lifetime | 20 years |
| Construction period | 3 years |
| Discount rate | 10% |
| Taxation | 20% |
| Contingency cost | 20% of fixed capital investment [19] |
| Working capital | 2 months of operating expenses [19] |
| Start-up capital | 10% of fixed capital investment [20] |
| Depreciation | 5% of fixed capital investment [19] |
| Supervisory and clerical labour | 30% of operating labour [18] |
| Maintenance and repairs | 3% of fixed capital investment [20] |
| Operating supplies | 15% of maintenance and repairs [20] |
| Laboratory charges | 30% of operating labour [19] |
| Patents and royalties | 1% of annual operating expense [20] |
| Overhead (plant and payroll) | 65% of sum of operating labour, supervisory and clerical labour, and maintenance and repairs [19] |
| Local taxes | 1% of fixed capital investment [20] |
| Insurance | 1% of fixed capital investment [20] |
| Administration cost | 25% of overhead [18] |
| Distribution and selling cost | 5% of annual operating expense [20] |
| Research and development cost | 5% of annual operating expense [20] |

Table 2
Prices of raw-materials, utilities, and catalysts.

| Raw materials, utilities, and catalysts | Price | Reference |
|---|-----------------------|-----------|
| Biomass feedstock (Spruce) ^a | 100 €/t | [21] |
| SO ₂ | 828.5 €/t | [22] |
| Sulphuric acid | 40 €/t | [23] |
| Hydrogen | 2500 €/t | |
| NaCl | 82.85 €/t | [22] |
| THF | 1657 €/t | [22] |
| HCl | 150 €/t | [23] |
| Lime | 239 €/t | [24] |
| Process water | 1 €/t | [25] |
| Cooling water | 0.24 €/t | [26] |
| Wastewater treatment | 0.34 €/m ³ | [27] |
| Gypsum disposal | 27.4 €/t | [28] |
| RuSn/C catalyst ^b | 456.3 €/kg | [29] |
| Cu ₂ Si ₂ O ₅ (OH) ₂ & Pd/SiO ₂ catalyst (1:2 mass proportion) ^b | 547.1 €/kg | [30] |
| Boiler chemicals | 5.99 €/kg | [24] |

^a includes transportation, pre-processing, storage, and handling cost.

^b 10% of the catalyst is refurbished every 6 months at a cost equivalent to 20% of its original value.

Table 3
Cost factors [20].

| Costs | Fraction of DEC |
|-----------------------------|-----------------|
| ISBL | |
| Equipment installation | 0.39 |
| Instrumentation & controls | 0.26 |
| Piping & electrical systems | 0.41 |
| OSBL | |
| Buildings | 0.29 |
| Yard improvements | 0.12 |
| Service facilities | 0.55 |
| Indirect costs | |
| Engineering and supervision | 0.32 |
| Construction | 0.34 |
| Legal expenses | 0.04 |
| Contractor's fee | 0.19 |

general operating expenses (GOE). The variable operating expenses include costs that account for raw materials, utilities, catalyst make-up, boiler chemicals, wastewater treatment and waste disposal. On the other hand, the fixed operating expenses include costs related to operating labour, supervisory and clerical labour, maintenance and repairs, operating supplies, laboratory charges, patents & royalties, overheads (plant & payroll), local taxes and insurance. The operating labor cost is calculated by considering 5 operators per shift position. The number of shifts is assumed as 5 with annual operator salary of around 56000 € [18]. The administrative, distribution & selling and research and development costs are included under general operating expenses.

The plant is operated continuously (8000 h) with an annual production capacity of 35 kt of GVL, 17 kt of 2-MTHF and 5 kt of 5-HMF. The plant lifetime is assumed to be 20 years with 100% equity financing. The FCI is assumed to be spent over a 3-year construction period, with 30%, 50% and 20% in the first (year -2), second (year -1) and third year (year 0), respectively. Working capital is invested in the final year of construction and recovered back at the end of the plant lifetime. In the first year of operation, the start-up capital is invested, and the plant operates with a production capacity of 50%, while incurring 100% of fixed operating costs and 50% of variable operating costs. Since the plant operation generates profit from year 1 onwards, depreciation can be charged and is calculated using straight-line depreciation with a 20-year recovery period. A discounted cash flow analysis is performed to estimate the minimum selling prices of the products (MSPs), net present value (NPV), internal rate of return (IRR) and payback period.

2.2. Process modeling

Aspen plus is utilized to model a commercial scale plant capable of processing 25000 kg/h of dry biomass. The sequential modular approach [31,32] is applied for the process simulation studies owing to its easy initialization and user-friendliness [33]. The process simulation flowsheet in the sequential modular approach is constructed by linking multiple process units, components, streams and selecting suitable units of measurement and thermodynamic methods [34]. The selected biomass is spruce with a composition of 44 wt% cellulose, 23.3 wt% xylose, 27.5 wt% lignin, 1.3 wt% acetate, 1.6 wt% ash and 2.3 wt% of other components such as extractives [35]. Typically, the moisture content of biomass is in the range of 5–35 wt%. Here, the moisture content is assumed to be 20 wt% to represent real feedstock more closely and the xylan composition is used to represent the hemicellulose sugars (xylan, arabinan, mannan and galactan) [36]. Hsiao et al. [37] simulated HMF purification by employing the NRTL-RK method. While simulating the production of platform chemicals from biomass Nitzsche et al. [38] and Olcay et al. [39] used the NRTL method for calculating the liquid phase activity coefficients and Henry's law for modeling the vapor phases. Based on these process simulation studies, the NRTL-RK (Non-Random Two-Liquid-Redlich-Kwong) property package coupled with Henry's law was chosen as the main thermodynamic model in this study. However, the Benedict-Webb-Rubin-Lee-Startling property package was employed to simulate the hydrogenation of furfural to 2-MTHF [30]. Aspen Plus lacks information regarding the physical properties of the main lignocellulosic components and therefore, these properties were defined from the database of the National Renewable Energy Laboratory (NREL), based on the work of Wooley and Putche [40]. The process flow diagram and mass balance are shown in Fig. 1 and Fig. 2, respectively.

2.2.1. Steam pre-treatment

One of the most efficient and widely utilized pre-treatment methods is steam explosion, which helps in extracting hemicellulose sugar monomers and by-products from lignocellulosic biomass. The benefits of this pre-treatment method include low capital investment, moderate energy consumption, and minimal environmental impact [41]. In the pre-treatment step, fresh spruce chips from the biomass handling section are transported to the pre-treatment stage, where they are impregnated with sulphur dioxide (SO₂) and subjected to high pressure steam (22 bar). The SO₂ and

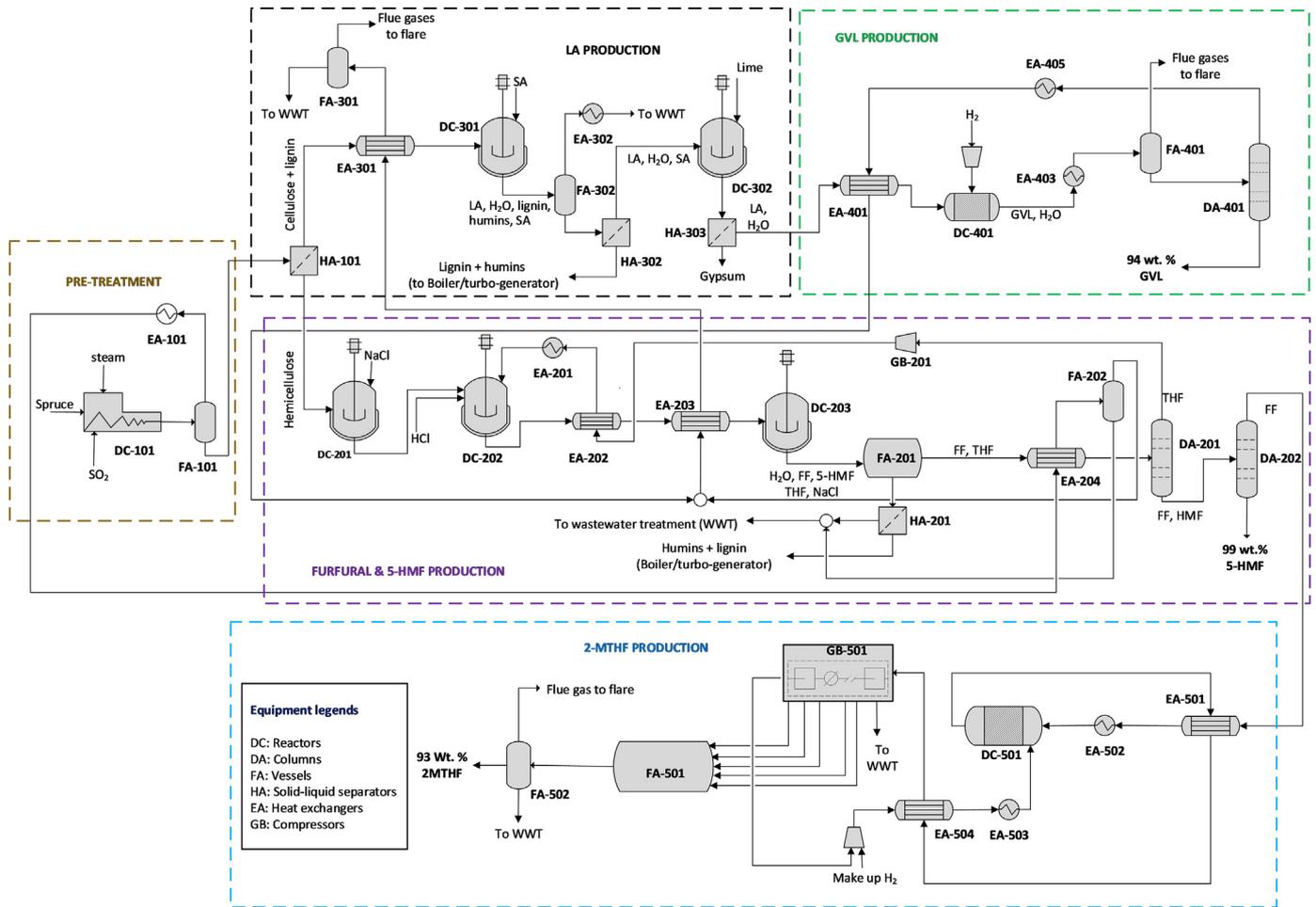


Fig. 1. Simplified process flow diagram for production of GVL, 2-MTHF and 5-HMF from biomass (spruce).

steam requirement is 2.4 kg SO₂/100 kg dry wood and 0.73 kg steam/kg of dry wood, respectively. The pre-treatment reactor (DC-101) is modelled as a fractional conversion reactor and the

operating temperature is 215 °C with a residence time of 3 min [42,43].

After pre-treatment, the pressure is reduced to 1 bar and the

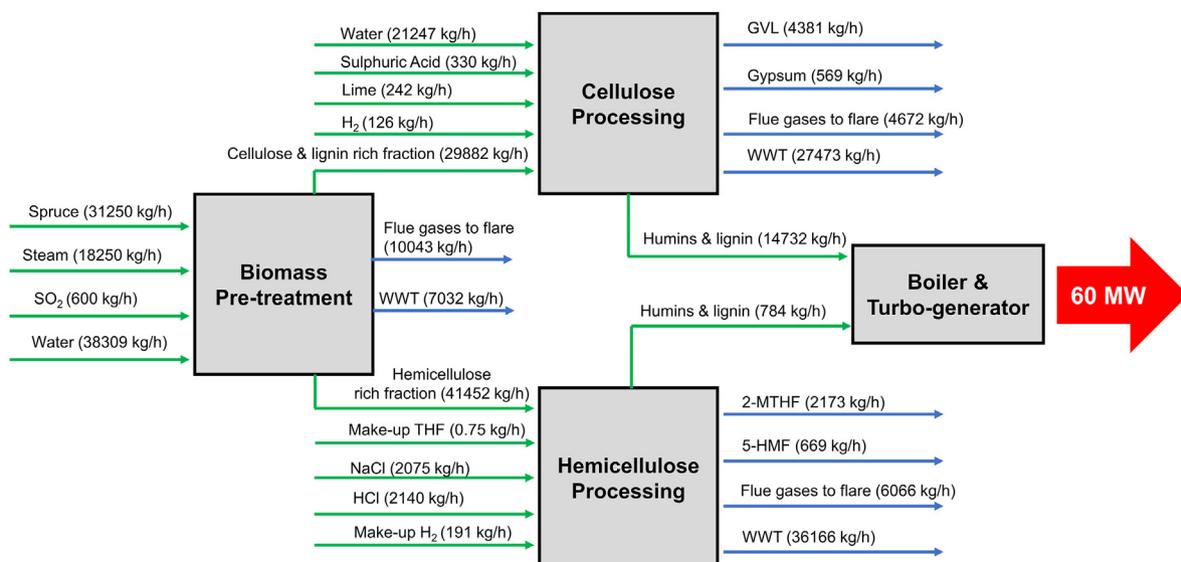


Fig. 2. Mass flow diagram for the different steps involved in the proposed bio-refinery concept.

Table 4
Reactions and yields for the processing steps involved in the proposed biorefinery concept.

| Conversion (%) | Conversion of component | Reaction |
|--|-------------------------|---|
| Pre-treatment [43] | | |
| 14 | Cellulose | Cellulose + H ₂ O → Glucose |
| 1.3 | Cellulose | Cellulose → 5-HMF + 2 H ₂ O |
| 70 | Xylan | Xylan + H ₂ O → Xylose |
| 15.5 | Xylan | Xylan → Furfural + 2 H ₂ O |
| 97 | Acetate | Acetate → Acetic acid |
| 10 | Lignin | Lignin → Soluble lignin |
| 100 | Ash | Ash → Soluble ash |
| LA production [39,46] | | |
| 100 | Cellulose | Cellulose + H ₂ O → Glucose |
| 75 | Glucose | Glucose → LA + FA + H ₂ O |
| 25 | Glucose | 9 Glucose → 4 HUM + 38 H ₂ O + 6 CO ₂ |
| 100 | Xylose | 27 Xylose → 10 HUM + 95 H ₂ O + 15 CO ₂ |
| GVL production [39] | | |
| 100 | LA | LA + H ₂ → GVL + H ₂ O |
| 100 | FA | FA → H ₂ + CO ₂ |
| Furfural & HMF production [39,49] | | |
| 100 | Xylan | Xylan + H ₂ O → Xylose |
| 80 | Xylose | Xylose → Furfural + 3 H ₂ O |
| 20 | Xylose | 27 Xylose → 10 HUM + 95 H ₂ O + 15 CO ₂ |
| 50 | Glucose | Glucose → 5-HMF + 3 H ₂ O |
| 50 | Glucose | 9 Glucose → 4 HUM + 38 H ₂ O + 6 CO ₂ |
| 2-MTHF production [30] | | |
| 97.1 | Furfural | Furfural + 4 H ₂ → 2-MTHF + H ₂ O |
| 1.4 | Furfural | Furfural + 2 H ₂ → 2 MF + H ₂ O |
| 0.3 | Furfural | Furfural + H ₂ → FFA |
| 0.3 | Furfural | Furfural → Furan + CO |
| 0.6 | Furan | Furan + 2 H ₂ → THF |

pre-treated biomass is sent to a flash unit (FA-101) operating at 103 °C. The energy from the resulting flash vapor is utilized as a source of heat, before sending it to the wastewater treatment (WWT) facility. The product from the flash unit containing solids along with the liquid is sent to a solid-liquid separator (HA-101). The solids are mainly comprised of cellulose and lignin and the liquid stream contains the hemicellulose sugars. The separator is a pneumapress filter in which the resulting solid cake consists of 55 wt% solids. A wash water to feed ratio of 1.16 is assumed to remove 96% of the solubilised hemicellulose sugars from the solid cake [44].

2.2.2. Levulinic acid (LA) Production

The pre-treated solids consisting of cellulose and lignin is introduced into the LA reactor (DC-301) and subjected to dilute acid hydrolysis in the presence of a mineral acid catalyst (H₂SO₄ (SA), 1.5 wt%) [39]. Cellulose is converted into an equimolar mixture of levulinic acid and formic acid (FA) with the formation of humins (HUM) due to the condensation of the unreacted sugars [45,46]. The LA reactor is modelled as a conversion reactor with a residence time of 60 min [46]. The operating temperature and pressure is 200 °C and 15.86 bar, respectively [39,46].

The product stream from the LA reactor is sent to a solid-liquid separator (HA-302) to remove insoluble lignin and humins. The separator is again a pneumapress filter with a cake washing efficiency of 96% and a wash water to feed ratio of 1.16 [44]. The

resulting solid stream contains 55% of solids and is sent to a boiler and turbogenerator to produce steam and electricity.

2.2.3. GVL production

Before introducing the LA rich stream into the GVL reactor (DC-401), the sulphuric acid present needs to be neutralized. The neutralization is carried out in the neutralization reactor (DC-302) by adding lime (Ca(OH)₂) and the resulting gypsum is separated using hydrocyclone and rotary drum filtration (HA-303) in series. It is assumed that the filtration removes 99.5% of the precipitated gypsum and the solids contain 20% liquid for easy handling of gypsum [44].

Following neutralization, the LA rich stream is introduced into the LA hydrogenation reactor (DC-401) operating at 220 °C and 35.85 bar, where levulinic acid is hydrogenated to GVL and water over a heterogeneous catalyst (RuSn/C) [46,47]. The formic acid present in the system decomposes into H₂ and CO₂, thereby providing additional hydrogen for the hydrogenation reaction [29,39]. The reaction and yields are shown in Table 4. The aqueous GVL rich stream is flashed (FA-401) at 1 bar and 75 °C to remove CO₂ and then introduced into a distillation column (DA-401) by which 94 wt% GVL is to be recovered as the bottom product.

2.2.4. Furfural & HMF production

The aqueous hemicellulose extract containing 10 wt% xylose [48] after biomass pre-treatment is saturated with NaCl (5 wt% of

Table 5
Energy requirements and carbon emissions for the process, before and after energy integration.

| Property | Before energy integration | After energy integration | % reduction |
|---------------------------|---------------------------|--------------------------|-------------|
| Heating utilities (MW) | 44.9 | 0.0 | 100% |
| Cooling utilities (MW) | 42.5 | 19.7 | 54% |
| Electricity (MW) | 5.8 | 0.0 | 100% |
| Total utilities (MW) | 93.2 | 19.7 | 79% |
| Carbon emissions (kt/yr.) | 85.0 | 48.2 | 43% |

the hemicellulose extract) [39]. The resulting sugar solution is mixed with organic solvent (THF), followed by the addition of 2 wt% acid catalyst (HCl) and introduced into the biphasic hydrolysis and dehydration reactor (DC-203) operating at 160 °C and 220 psig [39,49]. The mass ratio of THF to hemicellulose extract is 1.5 [49]. Under these process conditions, xylose undergoes biphasic dehydration to produce furfural (FF) and the unreacted sugars give rise to 5-HMF and humins [39,49].

Saturation with NaCl decreases the solubility of THF in the aqueous stream. THF addition to the aqueous phase facilitates extraction of products into the organic phase, thereby improving the selectivity for furfural before it can undergo any further degradation. The reactor outlet is sent to a decanter (FA-201) where 97% of the degradation products (furfural and 5-HMF) are recovered in the organic phase [39] and the aqueous phase obtained is filtered to remove the humins and lignin for energy generation and then sent to the wastewater treatment facility.

The organic stream containing THF, furfural and 5-HMF passes through a pressure reduction valve, where the pressure is reduced to 1 bar and is preheated before introducing into a series of distillation columns. In the first column (DA-201), pure THF is recovered in the top product and recycled back for re-use in the process. In the second column (DA-202), 95 wt% furfural is recovered in the top product and pure 5-HMF is obtained in the bottom product.

2.2.5. 2-MTHF production

The furfural produced in the previous step is vaporized and mixed with hydrogen such that molar ratio of hydrogen to furfural is 29:1. The resulting gas stream is then introduced into a hydrogenation reactor (DC-501) operating at 180 °C and 1.2 bar, wherein furfural is hydrogenated to 2-MTHF with a selectivity of 97.1%. The by-products formed during the reaction include 1.4% 2-methylfuran (2-MF), 0.3% furfuryl alcohol (FFA), 0.6% THF and 0.3% furan. The catalyst used is $\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_2$ and Pd/SiO_2 in a mass proportion of 1:2 with a weight hourly space velocity (WHSV) of 0.19 h^{-1} [50]. For recovery of 2-MTHF, the strategy presented by Silva et al. [30] is implemented. The gas stream leaving the reactor is used for preheating the furfural and hydrogen feed streams and in the process is cooled down to 77 °C. The cooled gas is introduced into a 7-stage compressor (GB-501). In each stage, the gas is compressed by a pressure ratio of 2 and cooled to 30 °C to recover the liquid product. A pressure drop of 0.05 bar is considered for the intercoolers between the stages. The hydrogen rich gas leaving the compressor is recycled back to the hydrogenation reactor for re-use, after pressure reduction.

The liquid knockout stream from stage 1 contains mostly water and is sent to wastewater treatment and the liquid knockout streams from the remaining stages are introduced into a 3-phase adiabatic separator (FA-502) operating at 1 bar. The vapor stream leaving the separator is sent to a stack for burning and the organic phase obtained contains 93 wt% 2-MTHF. Pure 2-MTHF can be obtained by dehydrating in molecular sieves, but this has not been considered in this study.

3. Results and discussion

Previous multiproduct biorefineries have explored the use of different biomass feedstock such as red maple wood [39] and birch [51,52]. In our article we have used spruce as a biomass feedstock owing to its easy availability in Finland, which is the intended location of the biorefinery.

The implemented integrated biorefinery results in low operational expenses on the account of efficient implementation of energy integration strategies to make it self-sustaining by reducing

the need for additional heating and electricity demand. This results in low manufacturing costs of the platform chemicals, thereby allowing them to compete with their petrochemical based counterparts. While several multiproduct refineries have explored the production of platform chemicals, very few have developed an integrated strategy which includes energy optimization and complete utilization of all biomass components (lignin, cellulose, and hemicellulose). Furthermore, the preliminary market assessment carried out in this study has led to the identification of key potential value-added applications for the platform chemicals produced in the biorefinery.

3.1. Energy analysis

In the proposed biorefinery concept, 25 t/h of dry biomass is processed, without energy integration, the process requires heating, cooling, and electricity demands of 44.9 MW, 42.5 MW and 5.8 MW, respectively. To improve the energy efficiency of the process, energy integration is accomplished by heat recovery between process streams using heat exchangers, through vapor recompression and by utilizing the activated energy savings tool available in Aspen Plus, which calculates the energy savings across the entire process and identifies targets for maximizing energy recovery to achieve the target heating and cooling.

The energy content of the biomass residues (lignin & humins) is estimated as 60.51 MW and is sufficient to satisfy the total heating and electricity demands of the energy integrated process, while also generating 1.75 MW of electricity that is sold to the grid for additional revenue. The biomass to electricity and biomass to heat generation efficiencies are assumed to be 30% [53] and 80% [54,55], respectively. Aspen energy savings tool also estimates the equivalent CO_2 emissions ($\text{CO}_2\text{-eq}$) originating from energy generation. Without energy integration, the $\text{CO}_2\text{-eq}$ emissions for the biorefinery would be about 85 kt $\text{CO}_2\text{-eq/yr}$. Upon implementing energy integration, the emissions were reduced to 48.2 kt $\text{CO}_2\text{-eq/yr}$, which translates to roughly 43% reduction. However, it is worth noting that the real emissions from energy use would vary depending on the source of the energy. For instance, when energy generation is done using renewable sources, the emissions would likely be even lower. The energy requirements and carbon emissions for the process, before and after energy integration are presented below in Table 5.

3.2. Capital and operating costs

Based on the simulation results and process parameters (temperature, pressure, mass flow rate and duty), the selection(mapping), sizing and purchased cost estimation of main process equipment such as heat exchangers, columns, reactors, compressors, pumps, conveyors, process vessels and storage tanks is performed using Aspen Process Economic Analyzer V11 (1st quarter 2018 pricing). Suitable exponential scaling expressions presented in the National Renewable Energy Laboratory (NREL) reports [44,55] are utilized for sizing and cost estimation of other equipment such as pre-treatment reactor, hydrocyclone and rotary drum filter, pneumapress pressure filter, boiler, turbo-generator, lime solids feeder, for which the sizing and cost evaluation could not be performed using Aspen Process Economic Analyzer.

A suitable material of construction is selected for each equipment depending on the prevailing process conditions. For instance, Monel is used in highly acidic and high temperature environments, SS6Mo is used in mild acidic conditions and SS316/316L is used for rest of the equipment [42]. All equipment and material costs are updated to 2020 prices in euro by considering the chemical engineering plant cost index (CEPCI) and currency conversion at the

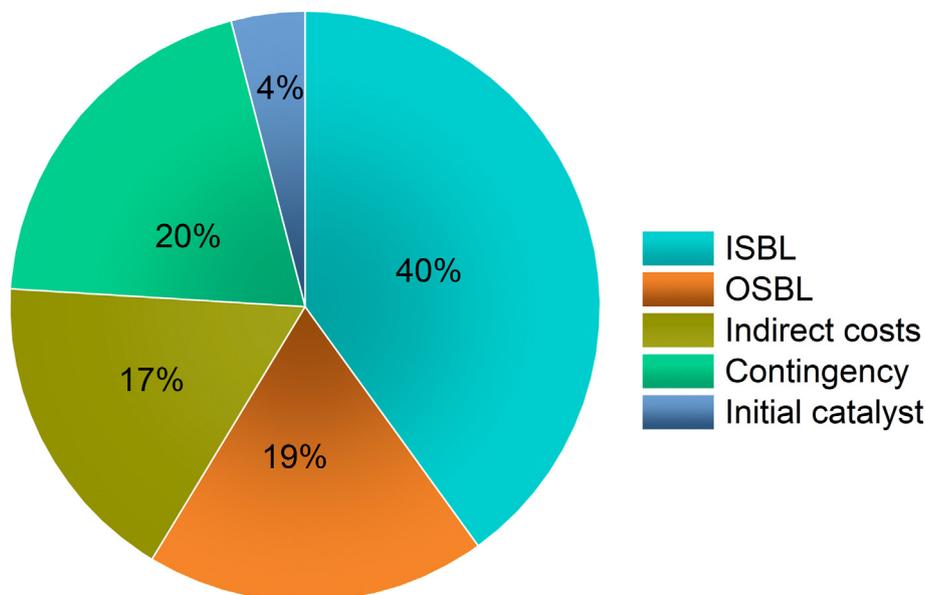


Fig. 3. Breakdown of fixed capital investment.

rate of 0.83 €/USD (6 months average). The total investment, calculated as the sum of fixed capital investment, working capital and start-up capital is estimated to be 256.72 M€ and the breakdown of the fixed capital investment is shown in Fig. 3.

The total operating cost, calculated as the sum of variable operating expenses, fixed operating expenses and general expenses is estimated as 65.39 M€/yr., as shown in Table 6. The variable operating cost, fixed operating cost, and general expenses account for 56%, 32% and 12% of the total operating cost, respectively. For the energy integrated process, the total heating and electricity demands are met by burning the biomass residues (lignin & humins) generated during the process. Therefore, the utility cost mainly includes the expenses arising from make-up cooling water, process water, and boiler chemicals. It is to be noted that the cooling water is recycled to the cooling tower for re-utilization

Table 6
Breakdown of annual operating costs.

| Component | Cost (M€/yr.) |
|------------------------------------|---------------|
| Variable operating expenses | 36.79 |
| Raw-material cost | 34.83 |
| Catalyst make-up | 0.37 |
| Utilities | 1.25 |
| Waste-water treatment | 0.21 |
| Gypsum disposal | 0.12 |
| Fixed operating expenses | 20.68 |
| Operating labour | 1.43 |
| Supervisory & clerical labour | 0.43 |
| Maintenance & repairs | 6.70 |
| Operating supplies | 1.01 |
| Laboratory charges | 0.43 |
| Patents & royalties | 0.65 |
| Overheads (plant & payroll) | 5.56 |
| Local taxes | 2.23 |
| Insurance | 2.23 |
| General operating expenses | 7.93 |
| Administration | 1.39 |
| Distribution & selling | 3.27 |
| Research & development | 3.27 |
| Annual operating costs | 65.39 |

within the process and the make-up cooling water for the cooling tower is assumed as 10% of the total cooling water requirement.

3.3. Minimum selling price and profitability analysis

Minimum selling prices (MSPs) of the products (GVL, 2-MTHF and 5-HMF) are estimated based on the total investment and annual operating costs by performing a discounted cash flow rate of return (DCFRR) analysis. MSPs are product prices that result in a net present value (NPV) of zero for a given discount rate. The market prices of the products are taken into consideration when estimating the MSPs and the solver tool available in Microsoft excel is utilized with the constraint that the calculated MSPs should be less than or equal to their existing market values. Based on this approach, the minimum selling prices for GVL, 2-MTHF and 5-HMF are estimated as 1.91 €/kg, 1.64 €/kg, and 1.93 €/kg, respectively and are compared with their average market prices as shown in Table 7.

The profitability of the process is evaluated based on the net present value (NPV), payback period (PBP), discounted payback period (DPBP) and internal rate of return (IRR). The equations used in the calculation of NPV are as follows:

$$\text{Gross profit} = \text{Revenue} - \text{Annual operating cost} \tag{2}$$

$$\text{Depreciation} = 0.05 \times \text{Fixed capital investment (FCI)} \tag{3}$$

$$\text{Net profit before taxers} = \text{Gross profit} - \text{Depreciation} \tag{4}$$

$$\text{Net profit after taxes} = (1 - \text{taxation rate}) \times \text{Net profit before taxes} \tag{5}$$

$$\text{Cash flow} = \text{Net profit after taxes} + \text{Depreciation} - \text{Capital expenses} \tag{6}$$

$$\text{Net present value (NPV)} = \sum_{n=1}^{n=t} \frac{\text{Cash flow}_n}{(1 + DR)^n}$$

Table 7
Comparison of estimated minimum selling price of products with their average market prices.

| Bio-refinery product | Minimum selling price (€/kg) | Average market price (€/kg) | Reference |
|----------------------------------|------------------------------|-----------------------------|-----------|
| γ-valerolactone (GVL) | 1.91 | 2.50 | [22,56] |
| 2-Methyltetrahydrofuran (2-MTHF) | 1.64 | 1.80 | [22,57] |
| 5-Hydromethylfurfural (5-HMF) | 1.93 | 2.00 | [22,58] |

where,

$Cash\ flow_n$ = Cash flow in year n; DR = Discount rate; t = Project lifetime in years.

The platform chemicals produced in this proposed biorefinery are sold at their average market prices, thereby generating a NPV of 153 M€ at the end of the project lifetime. The undiscounted payback and discounted payback periods are calculated as 5.4 and 8.9 years, respectively as seen in Fig. 4. The internal rate of return is determined by iterating the discount rate till the NPV reaches a value of zero at the end of the project lifetime and is found to be 15.9%. Since the NPV is positive and the internal rate of return is found to be more than the discount rate (10%), the project could be considered as viable and profitable.

3.4. Sensitivity and uncertainty analysis

A sensitivity analysis is carried out to evaluate the impact of key economic parameters such as annual operating costs, fixed capital investment, discount rate, taxation rate and catalyst price on the minimum selling prices of the products, as shown in Fig. 5. The parameters that are most sensitive are chosen for the sensitivity analysis. It was observed that annual operating cost, fixed capital investment and discount rate had the biggest impact on the MSPs. For instance, with a 25% increase in the annual operating costs, the MSPs of GVL, 2-MTHF, 5-HMF increased by 21.2%, 9% and 3.3%, respectively. On the other hand, the taxation rate and catalyst price had the least impact on the MSPs. With a 25% increase in the price of the catalyst, the MSPs of GVL, 2-MTHF and 5-HMF decreased by 0.6%, 0.3%, and 0.1%, respectively.

The uncertainty analysis is carried out via Monte Carlo simulation for the proposed biorefinery concept to quantify and evaluate the economic risk associated with the project. The Monte Carlo

simulation is performed in Microsoft Excel for 10000 iterations to understand how the uncertain parameters simultaneously interact with each other and influence the net present value. The simulation was accomplished by using random values generated from the triangular distribution for all the uncertain parameters presented in Table 8. For this biorefinery case, the upper and lower limits for the uncertainty parameters were chosen based on realistic ranges according to judgement and experience.

Based on the simulation study, the probability of loss (probability of NPV being less than or equal to 0) is estimated to be 17% with a mean NPV of around 130 M€, as seen from the NPV distribution shown in Fig. 6. The proposed biorefinery concept has a good possibility of being profitable when the uncertainty parameters are found to vary within suggested range.

3.5. Assessment of market potential of GVL, 2-MTHF and 5-HMF

Although GVL, 2-MTHF and 5-HMF are not currently widely used on an industrial scale, they offer significant market potential because of their properties. A preliminary assessment is carried out to identify the potential applications for each product based on the global market value and the compound annual growth rates (CAGR), as presented in Table 9. GVL has been used as a flavoring additive in the food industry for decades, however, since it still lacks a REACH (EU’s Registration, Evaluation, Authorisation and Restriction of Chemicals legislation) registration, the use is restricted and therefore new applications are assumed to hold larger market potential [59,60]. 2-MTHF is currently used in the syntheses of organometallics [13], however due to the very small market size, the potential for growth is limited and therefore this application has not been included in Table 9. As 2-MTHF has better properties compared to THF, it also has potential to replace THF in

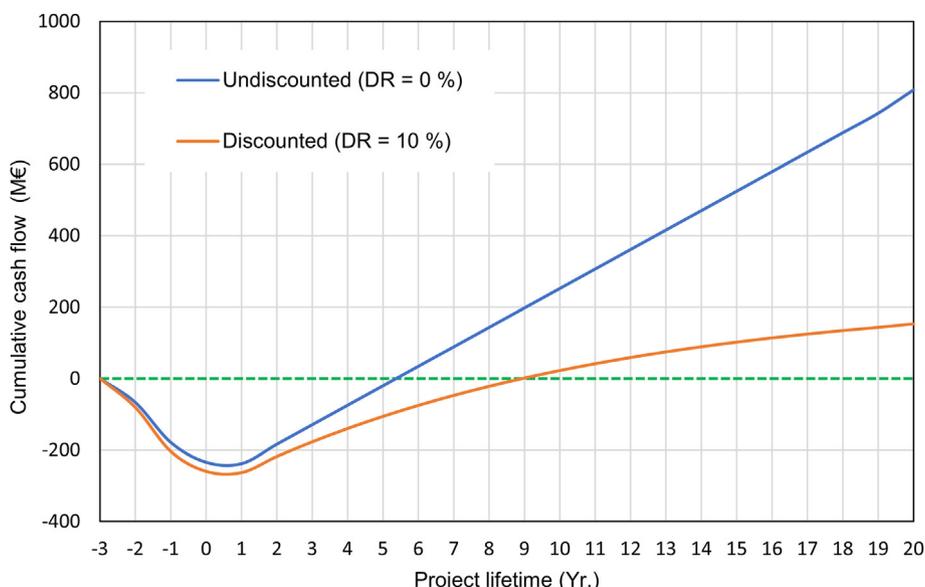


Fig. 4. Cumulative cash flow plotted as a function of the project lifetime.

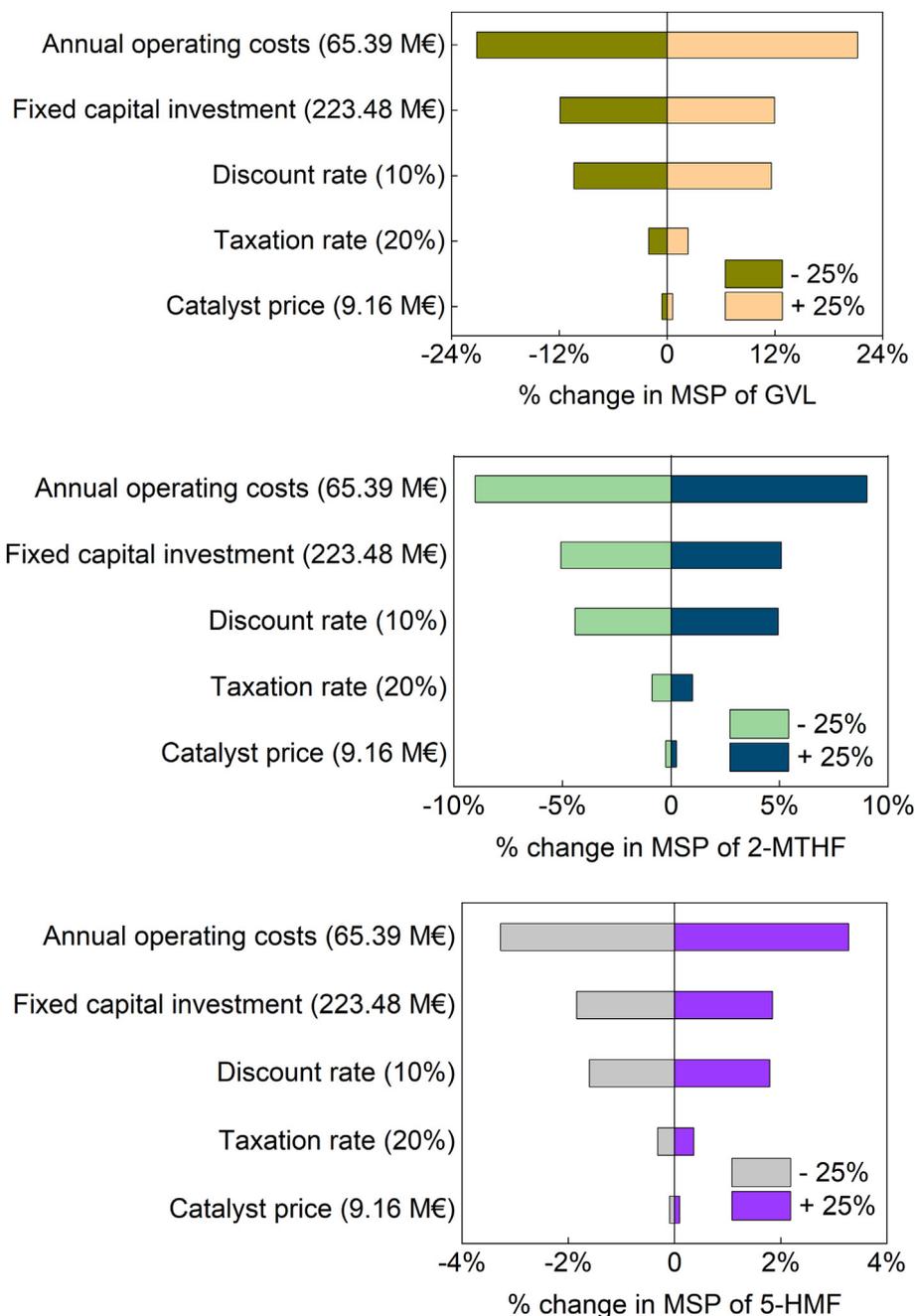


Fig. 5. Sensitivity analysis to evaluate the influence of key economic parameters on the MSP of GVL, 2-MTHF and 5-HMF.

several applications [13].

5-HMF is already utilized as a biochemical in small quantities [61] and is promising as a potential replacement of formaldehyde in phenolic resins [12]. It can also be used as a precursor in the manufacturing of polyethylene furanoate (PEF), which is considered as a bio-based alternative to polyethylene terephthalate (PET) [62]. With the global PET packaging market valued at 45.7 billion €, this is an opportunity for growth [63,64]. GVL, 2-MTHF and 5-HMF have suitable physical properties to be used as solvents [59,65], with an estimated market valuation of 18.1 billion € [66]. In addition, one of the most promising and attractive applications for all three products is as biofuels or biofuel additives [67,68], with the global biofuel market currently being valued at 112.9 billion € [69] and a CAGR of 2.2% [70].

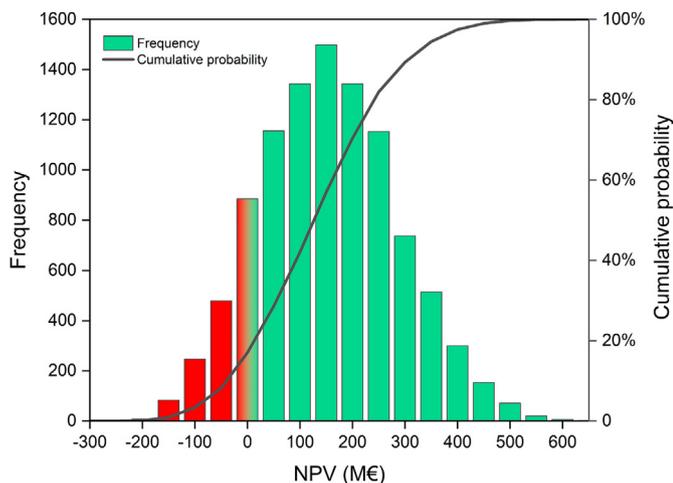
4. Conclusion

A biorefinery concept was developed to produce platform chemicals (GVL, 2-MTHF and 5-HMF) from lignocellulosic biomass (spruce) via aqueous phase processing. The process design was accomplished using rigorous process simulation models and energy integration was performed to minimize the utility requirements and the equivalent annual CO₂ emissions.

Based on the techno-economic assessment carried out, the MSPs of GVL, 2-MTHF and 5-HMF were estimated as 1.91 €/kg, 1.64 €/kg, and 1.93 €/kg, respectively. The low minimum selling prices of bio-based platform chemicals allow them to be used as a replacement for petrochemical based alternatives in varied applications, thereby advancing the field of renewable energy through

Table 8
Uncertainty parameters.

| Uncertainty parameter | Distribution function | Lower limit | Upper limit | Minimum value | Base value | Maximum value |
|-----------------------|-----------------------|-------------|-------------|---------------|------------|---------------|
| FCI (M€) | Triangular | −20% | 30% | 178.8 | 223.5 | 290.5 |
| OPEX (M€/yr.) | Triangular | −20% | 30% | 52.3 | 65.4 | 85.0 |
| Discount rate (%) | Triangular | −25% | 50% | 7.5 | 10 | 15 |
| Revenue (M€/yr.) | Triangular | −30% | 30% | 91.5 | 130.7 | 169.9 |

**Fig. 6.** NPV distribution from Monte Carlo simulation study. The bars coloured in red indicate NPV ≤ 0 .**Table 9**
Preliminary assessment of the market potential of GVL, 2-MTHF and 5-HMF.

| Products | Potential applications | Global market value (billion €) | CAGR (%) |
|---------------------|-------------------------|---------------------------------|----------|
| GVL | Flavor additives [60] | 7.6 [71] | 4.8 [72] |
| GVL, 2-MTHF & 5-HMF | Solvents [12,59,65] | 18.1 [66] | 6.6 [66] |
| 2-MTHF | THF replacement [13,65] | 2.2 [73] | 6.3 [73] |
| GVL, 2-MTHF & 5-HMF | Biofuels [67,68,74] | 112.9 [69] | 2.2 [70] |
| 5-HMF | Phenolic resins [12] | 2.2 [75] | 5.8 [75] |
| 5-HMF | PEF [62] | 0.02 [63] | 6.6 [63] |
| 5-HMF | PET packaging [62] | 45.7 [64] | 5.2 [64] |

effective biomass utilization for the development of renewable and circular bioeconomy solutions. The implementation of efficient energy integration strategies resulted in low operational expenses, thereby making the process viable and profitable by generating an internal rate of return of 15.9% at the end of the project lifetime. The sensitivity analysis revealed that reduction in the annual operating costs and fixed capital investment could have a positive impact on the profitability by further lowering the MSPs of the products. The economic risk associated with the project was evaluated based on an uncertainty analysis performed via Monte Carlo simulation and the probability of loss was estimated as 17% with a mean NPV of 130 M€, thereby further providing further validation for such a biorefinery concept to be adopted. In summary, the production of platform chemicals using the developed biorefinery approach can be considered as highly attractive based on the enormous market potential for use in applications such as biofuels and green solvents.

CRediT authorship contribution statement

Rahul Prasad Bangalore Ashok: Writing – review & editing,

Conceptualization, Methodology, Formal analysis, Writing – original draft, editing, Visualization. **Pekka Oinas:** Validation, Supervision, Writing – review & editing. **Susanna Forssell:** Writing – review & editing.

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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