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Geospatial environmental techno-economic assessment of pretreatment technologies for bioethanol production

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ABSTRACT

Second-generation biofuels, starting from lignocellulosic biomass, are considered as a renewable alternative for fossil fuels with lower environmental impact and potentially higher supply and energy security. The economic and environmental performance of second-generation bioethanol production from corn stover in the European Union (EU) is studied, starting in Belgium as base case. A comparative environmental techno-economic assessment has been conducted, with process simulations in Aspen Plus and corn stover availability data in thirteen EU countries to calculate minimum ethanol selling prices (MESP) and Greenhouse gas emissions (GHGe). In this analysis, the emphasis is on the comparison of different pretreatment technologies, namely (i) dilute acid, (ii) alkaline, (iii) steam explosion and (iv) liquid hot water. Dilute acid showed the best economic and environmental performance for the base case scenario. Within the EU, Hungary and Romania presented the lowest MESP for the steam explosion model at 0.39 and 0.43 EUR/L respectively. Poland showed the lowest GHGe, at 0.46 kg CO_2eq/L for the alkaline model, mainly due to the avoided product allocation on electricity and its high carbon intensity in the electricity generation sector. The second lowest GHGe were obtained in France for the dilute acid model and are attributed to its low agricultural emissions intensity. This study identifies a location-dependence of the economic and environmental performance of pretreatment technologies, which can be extrapolated from the

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EU to other large regions around the world and should be taken into consideration by decision-makers.

HIGHLIGHTS

- EU geospatial environmental techno-economic assessment of lignocellulosic ethanol
- Location-dependence of pretreatment technology performance
- Biorefinery scale and biomass cost drive the MESP
- Lowest MESP and GHGe for dilute acid for most case studies
- Alkaline lower GHGe than dilute acid when high carbon intensity in the power sector

KEYWORDS

Lignocellulosic biomass, pretreatment, advanced biofuels, cellulosic ethanol, techno-economic assessment, environmental impact assessment

NOMENCLATURE

ABBREVIATIONS

CAPEX: Capital expenditure

ETEA: Environmental techno-economic assessment

FCI: Fixed capital investment

GHGe: Greenhouse gas emissions

LCA: Life cycle assessment

MESP: Minimum ethanol selling price

NREL: National Renewable Energy Laboratory

OPEX: Operational expenditure

TEA: Techno-economic assessment

SYMBOLS

$CEPCI_{2021}$: CEPCI in 2021

$CEPCI_{ref}$: CEPCI in reference year

C_{new}: new case equipment costs (EUR)

C_{ref}: base case equipment costs (EUR)

S_{base}: base case equipment size

S_{new}: new case equipment size

n: scaling exponents

1. INTRODUCTION

Switching to renewable energy sources is seen as an alternative to secure future energy supply, while reducing greenhouse gas emissions (GHGe) and the dependency on fossil fuel sources [1]. The transport sector is one of the major players in global GHGe, accounting for more than a quarter of the total emissions in 2019 [2]. Bioethanol is an alternative transportation fuel, which can be used as a mixture with gasoline in existing gasoline vehicles [3].

Biowaste, agricultural and forestry residues can be used as feedstock to produce second-generation, also known as advanced biofuels [4]. Lignocellulosic biomass is an abundant source that can be used for such purposes [5]. These biofuels have the advantage of not competing with the food supply chain [6], while they have been proven to have lower GHGe compared to the traditional fossil fuels [7]. However, an additional process step is required when handling lignocellulosic biomass: the pretreatment. This process aims at breaking the complex lignocellulosic matrix and has a big impact on the economic profitability of the biorefinery [5]. Various pretreatment methods have been investigated over the years, mainly categorized as physical, chemical, physicochemical and biological, while combinations of those have also been studied [8].

One of the most thoroughly studied pretreatment methods is the dilute acid pretreatment, which requires the use of an acid catalyst, usually sulfuric acid. Acid loading, temperature and residence time are some of the parameters that contribute to the disruption of the lignocellulosic structure [9]. This method is highly effective in the degradation of hemicellulose to monomeric sugars. However, the production of inhibitors, the acidic conditions and special equipment required are some of the bottlenecks of this method [8]. Another chemical pretreatment method is the alkaline pretreatment, which targets the removal of lignin. This method removes lignin without further degrading carbohydrates and does not require as harsh conditions as acid pretreatment [10]. Steam explosion is a physicochemical method that requires high temperature and short residence time. Biomass is treated with high pressure steam for a few minutes and then pressure is rapidly released, which causes an explosive decompression and disruption of the lignocellulosic structure. High efficiency in hemicellulose hydrolysis and lack of chemical reagents are some of the advantages while, on the other hand, the incomplete lignin removal and the formation of inhibitors are some limiting factors [11]. Liquid hot water (or hydrothermal) is another physicochemical pretreatment technology which requires water at high temperature, thus creating acidic conditions that promote the solubilization of hemicellulose. This method does not require any chemicals but the high energy and water consumption along with the degradation of sugars to inhibitory compounds are recognized as bottlenecks [12].

The EU has recently proposed the “Fit for 55” package, aiming at a 55% reduction of greenhouse gas emissions by 2030 and at least 40% share of renewable energy in overall energy consumption [13]. Despite the current energy targets and the continuous efforts to improve the pretreatment processes, advanced biofuels production within EU is still limited. Notable, only one third of the liquid biofuels biorefineries operating in Europe in 2021 were producing advanced biofuels [14]. Therefore, the identification of the most cost-effective pretreatment method, with respect to its bioethanol production and environmental performance is crucial.

Techno-economic assessment (TEA) and life cycle assessment (LCA) studies are widely performed to evaluate the production of biofuels, but a combination of these two is quite limited [15]. A literature review was performed in Web of science, using “ethanol”, “techno-economic” and “environmental” as search terms, for relevant published studies during 2018-2023. Since the scope of this study is restricted to pretreatment technologies, which are applied within a lignocellulosic biorefinery, addressing both economic performance and environmental impact simultaneously, the 180 initial results were narrowed to 19, summarized in Table 1.

All of these studies use economic and environmental indicators to compare different biorefinery configurations based on the processes applied and/or final products. García-Velasquez et al. [16] have performed a comparative analysis between conversion pathways, while different energy supply systems within a bioethanol plant have been investigated by Nwai & Patel [17]. Moreover, the performance of a duckweed-fed biorefinery coupled with wastewater treatment plants has been evaluated by Calicioglu et al. [18].

The effects of different co-products, such as lactic acid and methanol [19], pectin and polyphenols [20], xylose sugars and adhesive [21], syrup from C5 sugars [22], xylitol and antioxidants [23] in combination with bioethanol have also been studied. The use of distiller’s grains with solubles has been evaluated by DeRose et al. [24] in a multi-product biorefinery. Different plant residues for animal feed, starch, lactic acid and bioethanol have also been studied by Serna-Loaiza et al. [25]. The effect of process inputs, such as cellulase hydrolytic activities [26], surfactants [27], solids loading [28] as well as raw biomass forms (loose or pellets) [29] has been examined on the economic and environmental performance of biorefineries. Novel pretreatment technologies such as low-moisture anhydrous ammonia [30] and solvolysis with methanol [31] have also been evaluated.

Table 1. Literature review on TEA-LCA studies for lignocellulosic bioethanol production (*Calculated assuming 7920 working hours per year).

Authors	Pretreatment technology	Feedstock	Scale (dry t biomass/y)	Biorefinery location
da Silva et al. [32]	Dilute acid, Liquid hot water, Steam explosion, Ammonia fiber explosion, Organosolv	Corn stover	768,240	Unspecified
García-Velasquez et al. [16]	Steam explosion	Pinus Patula	330,000*	Colombia
Gumte et al. [33]	Acid hydrolysis, Steam explosion, Ionic liquids	Corn stover, bamboo grass, bagasse, wood chips	330,000-3,300,000*	India
Mandegari et al. [19]	Steam explosion with SO_2	Bagasse	421,000	Unspecified
Manhongo et al. [20]	Shredding, milling, conditioning with steam	Mango waste	99,000*	South Africa
Nickel et al. [26]	Acid catalyzed steam explosion	Wheat straw	504,000	Sweden
Pandey et al. [29]	Soaking in aqueous ammonia	Corn stover	660,000*	Unspecified
Pang et al. [21]	Dilute acid	Corncob	157,500	China
Kadhum et al. [27]	Dilute acid	Banagrass	60,000	Maui island, USA
Lopez-Hidalgo et al. [34]	Dilute acid, Autohydrolysis & dilute acid	Wheat straw & corn stover	165,000*	Mexico
Vaskan et al. [22]	Dilute acid, liquid hot water	palm empty fruit bunches	461,736*	Brazil

DeRose et al. [24]	Dilute acid	Distiller's grains with solubles	277,530*	USA
Servian-Rivas et al. [23]	Steam explosion	olive tree pruning waste	33,000*	Spain
Serna-Loaiza et al. [25]	Dilute acid	Cocoyam residues	198–990,000*	Colombia
Calicioglu et al. [18]	Liquefaction	Duckweed	7,210	USA
Oliveira and Rosentrater [30]	low-moisture anhydrous ammonia	Sugarcane bagasse	330,000-3,300,000	Unspecified
Nwai & Patel [17]	Dilute acid	Corn stover	833,336	South Africa
Obydenkova et al. [31]	Solvolysis with methanol	Forest residues	489,750	the Netherlands
Solarte-Toro et al. [28]	Acid	Olive tree pruning biomass	30,000	Spain

A recently published review on integrated TEA and LCA studies on process design by Mahmud et al. [35], indicated the importance of such studies, revealing the relations between technical, economic and environmental performance. However, such studies are scarce, while a lack of a consistent methodological framework is identified. Therefore, despite the application of different pretreatment technologies in each study, a comparison cannot be accurately done. The need for a comparative environmental techno-economic assessment (ETEA) on pretreatment methods is recognized.

Out of the reviewed studies, only two have performed a comparison between pretreatment technologies. Da Silva et al. [32], investigated the economic and environmental performance of five pretreatment technologies, by simulating a large scale bioethanol plant and applying a methodology called economic value and environmental impact (EVEI). Dilute acid and autohydrolysis followed by dilute acid pretreatment methods have been compared by Lopez-Hidalgo et al. [34] for two different biomass types, while investigating the effect of a genetically engineered E-coli.

More than half of the studies in Table 1 evaluated the performance of large scale biorefineries, over 330000 t/y (or 1000 t/day), while only three investigated the effect of the plant capacity in the overall performance. Also, almost all of these case studies were conducted for a single biorefinery location, without investigating its effect in the performance of different biorefinery configurations. Gumte & Mitra [33] have optimized supply chain networks from raw material suppliers to retailers in order to meet India's ethanol blending fuel targets, by taking into consideration the geographical location of the different network layers. Four different biomass types have been studied in order to maximize the net present value, while accounting for carbon credits from GHGe. However, each biomass type is directly linked to a unique production pathway, thus the choice of the best performing conversion technology is based solely on the agricultural production of the examined region.

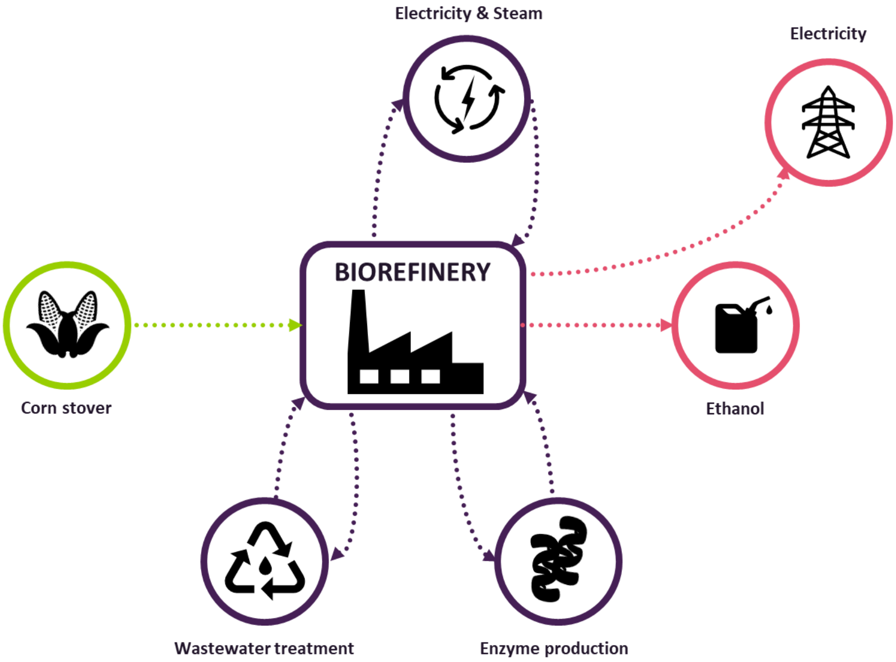

Figure 1. Schematic overview of the investigated bioethanol plant.

This study aims to fill in the literature gap by applying a transparent ETEA framework, developed by Thomassen et al. [36], in a comparative study between different pretreatment technologies. Four common pretreatment methods, i.e. dilute acid, alkaline, steam explosion and liquid hot water are investigated, by developing simulation models and performing a comparative ETEA. The simulated biorefinery is close to a real commercial plant, as it includes additional processes required, such as wastewater treatment and enzyme production, as described in Figure 1. The framework is first applied for a base case study in Belgium, which has not been investigated yet in literature, by taking into consideration the available domestically produced corn stover as feedstock. As a result of biomass availability limitations, the biorefinery is considered as small scale compared to most of the reviewed studies of Table

1 (over 1000 dry t/d), but in the context of the Belgian territory this could be considered as a large scale biorefinery. The Minimum ethanol selling price (MESP) and GHGe for each pretreatment model are calculated initially for the base case, identifying the key parameters with a significant influence in the biorefinery performance. Then, a geospatial variance of these parameters is conducted for countries within the EU, due to the scarcity of studies performed in the continent. Given the importance of the plant capacity, thirteen case studies in EU countries with a bigger biomass production than the base case (i.e. Austria, Bulgaria, Croatia, Czech Republic, France, Germany, Greece, Hungary, Italy, Poland, Romania, Slovakia, Spain) [26] are chosen, by using European spatial data on corn stover supply and price, tax rate, salaries, by-product selling price, GHGe during biomass cultivation and electricity generation carbon intensity. This analysis identifies the relation between pretreatment technologies performance, both economic and environmental, and biorefinery locations and provides additional insights on (i) the most promising pretreatment technologies within the EU and (ii) where in the EU second-generation bioethanol plants show the most potential, which can be valuable outcomes for decision-makers within the EU.

2. MATERIALS AND METHODS

A comparative ETEA is carried out to assess the economic and environmental performance of a bioethanol plant located within the EU, based on different pretreatment methods. First, the assessment is carried out for a base case, that being a bioethanol plant processing corn stover in Belgium. Based on the obtained results, the assessment is conducted for 13 more EU countries. The ETEA framework (Figure 2) applied in this study consists of five steps [37]: (i) the definition of the goal and the scope; (ii) a market study on commodity prices and volume; (iii) process flow diagram development and mass and energy balance calculations using ASPEN Plus; (iv) an economic and environmental impact assessment; (v) interpretation of the results, identifying key performance parameters, by performing an economic global sensitivity analysis (only for the base case) as well as a plant capacity break-even point analysis.

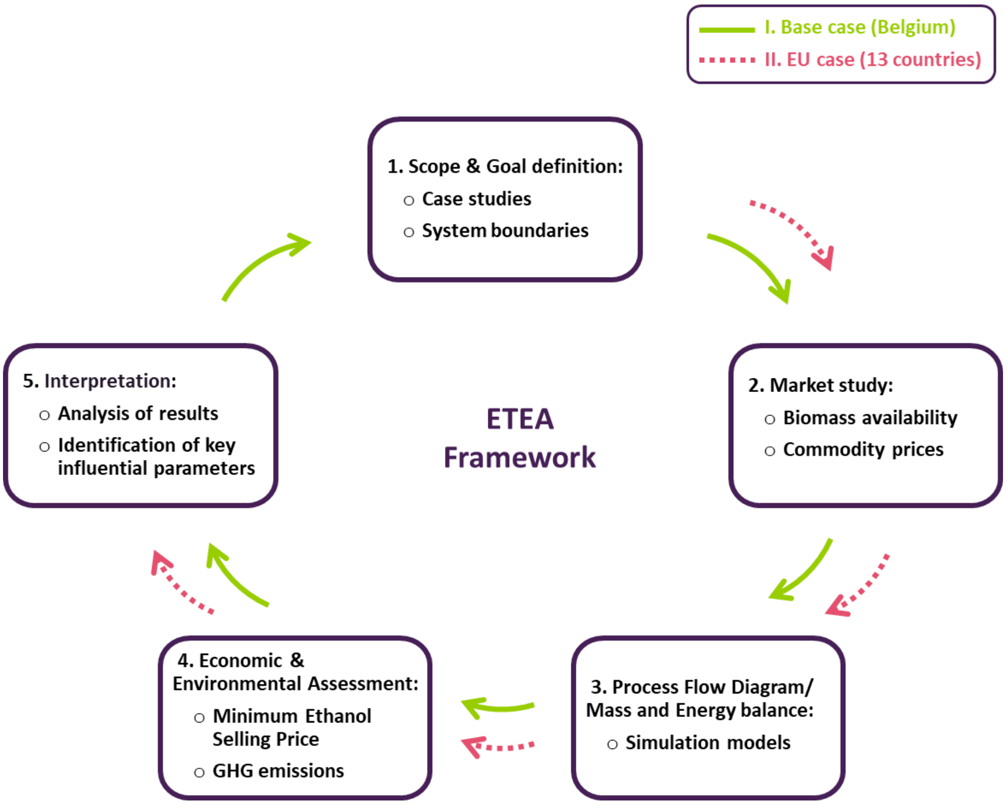

Figure 2: Environmental Techno-Economic assessment (ETEA) framework applied in this study [37].

2.1 Goal and Scope definition

An integrated techno-economic and environmental impact assessment is conducted. The goal of the economic assessment is to evaluate the economic performance of each biorefinery configuration by calculating the MESP, while the environmental assessment aims at measuring the environmental impact by calculating the GHGe as CO_2 equivalents. The scope of both assessments covers a large scale commercial biorefinery with bioethanol as the final product for application in the transport sector and 1 L of final product as the functional unit. A base case scenario is applied in Belgium, using its results to define thirteen more case studies within the EU, by geospatially varying major parameters. The system boundaries for the TEA are gate-to-gate, as corn stover is assumed to arrive at the plant-gate ready for the pretreatment process. On the other hand, a cradle-to-gate approach is chosen for the environmental assessment, due to the different biomass conversion yields between the simulation models, indicating a different biomass contribution to the final indicator per L bioethanol produced. The main purpose of this study is to compare the different pretreatment technologies within a commercial biorefinery plant, thus the end-use of the biofuel is left out of the scope. The pretreatment technology does not affect the quality of the final biofuel, as this is kept the same for all models, at 99.5 % (w/w) purity.

2.2 Market study

The first step is to investigate the biomass availability. National data on agricultural production and residue-to-crop rates are used to estimate annual agricultural residues production. The final residue availability for biofuels production is calculated, by taking into consideration that a part of these residues should remain in the field for soil quality preservation, while another part is already exploited for other uses.

The plant-gate biomass cost is estimated based on farm-gate national costs, including transportation, storage and feed-handling costs. Cost of chemicals, utilities and disposal, as well as product and by-product selling prices are investigated in this step.

2.3 Process model development

Simulation models are developed for all processes and mass and energy balances are derived, using Aspen Plus® v.12.1 [38], according to the biochemical model developed by the National Renewable Energy Laboratory (NREL) [39]. This model is widely used in literature as a base case because of its detailed analysis. The simulation, as shown in Figure 5, includes the following sections: pretreatment, separate enzymatic hydrolysis & fermentation, enzyme production, product recovery, wastewater treatment, storage, energy generation and utilities. Due to the non-ideality of the polar compounds used in the simulation, the non-random two liquid (NRTL) activity coefficient model is chosen [40].

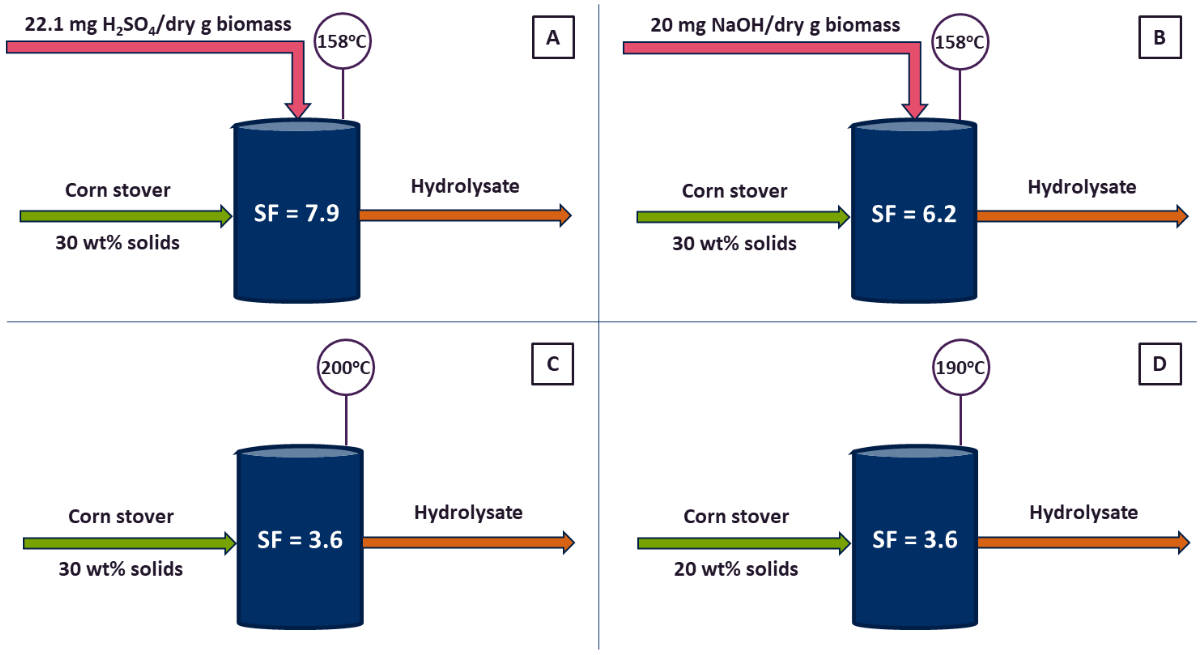

Figure 3. Pretreatment reactor conditions and severity factors (SF) for the (A) dilute acid, (B) alkaline, (C) Steam explosion, (D) Liquid hot water models.

A simulation model is developed for each pretreatment method, by keeping all of the rest process units and conditions the same as the NREL model. There is thus a consistent basis for comparison, as only the pretreatment area is different between the four models.

Sulfuric acid and sodium hydroxide are chosen for the dilute acid and alkaline pretreatment respectively. Solids loading is lower for the liquid hot water model, due to operational constrains [41]. Instead of separation and water washing units, commonly applied in small-scale experiments [42], chemical conditioning to neutral pH with ammonia or sulfuric acid is chosen for all models, due to the large volumes present in the studied simulations. Based on the pretreatment conditions, the severity factor is calculated for all models according to Pedersen et al. [43], as presented in Figure 3. Table *2* includes the pretreatment fractional conversions chosen for each model. The reaction conversions for the dilute acid pretreatment are the same as the NREL model [39], while the severity factors are used to estimate the reaction yields, according to lab-scale experiments for the rest of the models.

Table 2. Pretreatment fractional conversions (%) used in ASPEN Plus models [44–46].

Products	Pretreatment method			
	Dilute acid	Alkaline	Steam explosion	Liquid hot water
Glucose	9.90	3.00	5.00	2.00
Gluco-oligomer	0.30	0.30	0.60	0.60
Xylose	90.0	3.00	60.0	50.0
Xylo-oligomer	2.40	7.20	4.80	7.20
Soluble lignin	5.00	60.0	5.00	5.00
HMF	0.30	0.01	0.90	0.10
Furfural	5.00	0.01	15.0	0.15

2.4 Process economics

The MESPs, expressed in EUR 2021, are calculated for the four biorefinery configurations, each having a different pretreatment section. To calculate the MESP, capital expenditures (CAPEX) and operational expenditures (OPEX) need to be calculated based on the process model that has been developed. A plant with a lifetime of 20 years and 8000 annual operating hours, starting its operation in 2021 is assumed. A linear depreciation method is chosen for a depreciation period of 7 years for the general plant and 20 years for the energy generation area [47], while national tax rates are taken into consideration for the calculation of revenues.

The CAPEX consists of the fixed capital investment (FCI), the working capital and land costs. A 15% discount rate is applied [48], while working capital is taken as 5% of the FCI [39] and land cost as 2% of the FCI [49].

The FCI includes total direct costs (equipment cost and additional costs for warehouse, site development and piping) and total indirect costs (fringe benefits, burdens, construction insurance, field expenses, construction fees, project contingency and other indirect costs) [39]. Equipment cost data, installation factors and scaling exponents n from the NREL [39] are used for the equipment costing of all plant sections, except the pretreatment reactors which are based on literature [50]. These equipment costs are adjusted to the cost year (2021) using the chemical engineering plant cost indices (CEPCI) [51], as indicated in Equation (1).

$$C_{new} = C_{base} \cdot (\frac{S_{new}}{S_{base}})^{n} \cdot (\frac{CEPCI_{2021}}{CEPCI_{ref}}) \tag{1}$$

Where C_{new} and C_{base} are the new and the base case equipment costs, S_{new} and S_{base} the new and base case equipment sizes, n the scaling exponents and C_{2021} and C_{ref} the CEPCI in 2021 and in the reference year respectively.

The OPEX consists of the variable and fixed operating costs. Feedstock, raw material, utility and waste disposal prices are used to calculate the variable operating costs. The fixed operating costs (operator wages, maintenance, supervision, overhead, property taxes and insurance) are estimated based on average national salaries. The number of operator shift positions is based on the work of Sinnot and Towler [52].

2.5 Environmental Impact Indicator Calculation

The environmental impact of each pretreatment method is evaluated by calculating the GHGe, as CO_2 equivalents. The greenhouse gases and their equivalence to CO_2 are taken from the EU Renewable Energy Directive II (RED II) [4]. This indicator includes emissions from biomass cultivation at a national level, biomass drying, handling, storage and transportation to the plant, as well as during bioethanol production. For the biomass cultivation, an economic allocation is chosen while the avoided product allocation is applied for the by-product, as the excess electricity produced is assumed to be sold to the local grid. The electricity mix of each case study is taken into consideration. Emission savings from biomass sequestration are not accounted, as commonly done in biofuels cradle-to-gate environmental assessments [53].

2.6 Interpretation

The interpretation step consists of conducting a global sensitivity analysis for the base case, as well as a feedstock break-even point analysis for different country-based biorefineries within the EU.

First, a global sensitivity analysis is performed in order to simultaneously investigate the impact of several economic parameters to the MESP. The Monte Carlo method [54] is chosen to randomly sample the selected parameters and run multiple evaluations to calculate the model output. The variables selected are the FCI, discount rate, tax rate, biomass cost, chemicals cost and by-product selling price. Triangular distribution is chosen for all variables based on a ±20% variation range from the base case, 5000 model evaluations are performed and the contribution to variance of MESP is calculated for each variable and simulation model.

Finally, a break-even point analysis is carried out in order to calculate the minimum plant capacity needed to reach a net present value (NPV) of zero. All relevant variables required for the net present value calculation are correlated with the feedstock inflow, through a regression analysis. The FCI and plant capacity are associated by equation (1), where cost refers to FCI and size to plant capacity. A scaling factor of 0.6 is chosen [55]. The analysis is performed for all simulation models and case studies.

3. CASE STUDIES

3.1 Biorefinery locations

For the base case, 519 kt of corn stover were produced in Belgium in 2020 [56], assuming a production rate of 1 dry kg per dry kg of corn grain [57]. A 30% of the total corn stover is assumed to be available as a feedstock for biofuels production [58], which corresponds to 156 dry kt/year. Detailed corn stover composition is taken from Humbird et al. [39], adjusting moisture content to fit the average moisture of European corn stover [59].

Belgian corn stover production is taken as a minimum threshold, in order to define the rest of the case studies. Therefore, thirteen EU countries are chosen [60], applying the same assumptions as in the base case (Figure 4 (A)).

3.2 Economic assessment parameters

The corn stover farm-gate price [60] is assumed to be half of the final plant-gate price [61] (Figure 4 (B)). The costs of chemicals, utilities and disposal are assumed to be the same within the EU, as presented in Table *3*. Producer price indices for chemicals are used when needed to update prices to 2021. Bioethanol price is taken as 0.51 EUR/L for 2021 within the EU market [62], while wholesale electricity by-product prices are used for each case study [63,64].

Table 3. Raw materials and utilities cost in 2021 EUR

Material	Value	Unit	Source
Anhydrous ammonia	602	EUR/t	[65]
Ash disposal	45	EUR/t	[52]
Boiler chemicals	5.1	EUR/kg	[39]
Cooling tower chemicals	3.1	EUR/kg	[39]
Corn steep liquor	59	EUR/t	[39]
Diammonium phosphate	739	EUR/t	[65]
Fresh water	0.30	EUR/t	[52]
Denaturant	0.48	EUR/L	[66]
Glucose syrup	459	EUR/t	[65]
Host nutrients	840	EUR/t	[39]

Lime	149	EUR/t	[65]
Sodium hydroxide	525	EUR/t	[65]
Sorbitol	1.50	EUR/kg	[65]
Sulfur dioxide	528	EUR/t	[65]
Sulfuric acid	58	EUR/t	[65]

Tax rates for all case studies are presented in Figure 4 (C) [67]. Wages for the base case are taken from data on the Belgian chemical industry [68], while average national salaries [69] are used for the rest of the case studies (Figure 4 (D)).

3.3 Environmental assessment parameters

Average GHGe during biomass cultivation are taken from the statistical database of the Food and Agriculture Organization (FAOSTAT) for each case study, based on the latest available data on cereals cultivation during 2020 [70]. The emissions are converted from kg CO_2eq/kg biomass to kg CO_2eq/dry kg biomass, according to the EU RED II (Figure 4 (E)) [4]. GHGe during biomass drying, handling, storage and transportation are calculated based on average European data [71]. GHGe factors for electricity are based on the electricity mix of each studied country in 2021 (Figure 4 (F)) [72]. The rest of the emission factors are taken as average from European data [71], while EcoInvent [73] is used for any missing data, as presented in Table *4*.

Table 4. Emission factors

Input	Value	Unit	Source
Ammonia	2.3513	kg CO_2/kg	[71]
Antifoam	3.2748	kg CO_2/kg	[71]
Corn steep liquor	0.00913	kg CO_2/kg	[73]
Diammonium phosphate	0.6744	kg CO_2/kg	[71]
Diesel	0.0951	kg CO_2/MJ	[71]
Gasoline supply	0.01988	kg CO_2/MJ	[71]
Glucose	1.33	kg CO_2/kg	[73]
Light heating oil	0.488	kg CO_2/kg	[73]
Lime	1.14	kg CO_2/kg	[73]
Natural gas	0.0097	kg CO_2/MJ	[71]
Sodium hydroxide	0.5297	kg CO_2/kg	[71]
Sulfur dioxide	0.0533	kg CO_2/kg	[71]
Sulfuric acid	0.2175	kg CO_2/kg	[71]

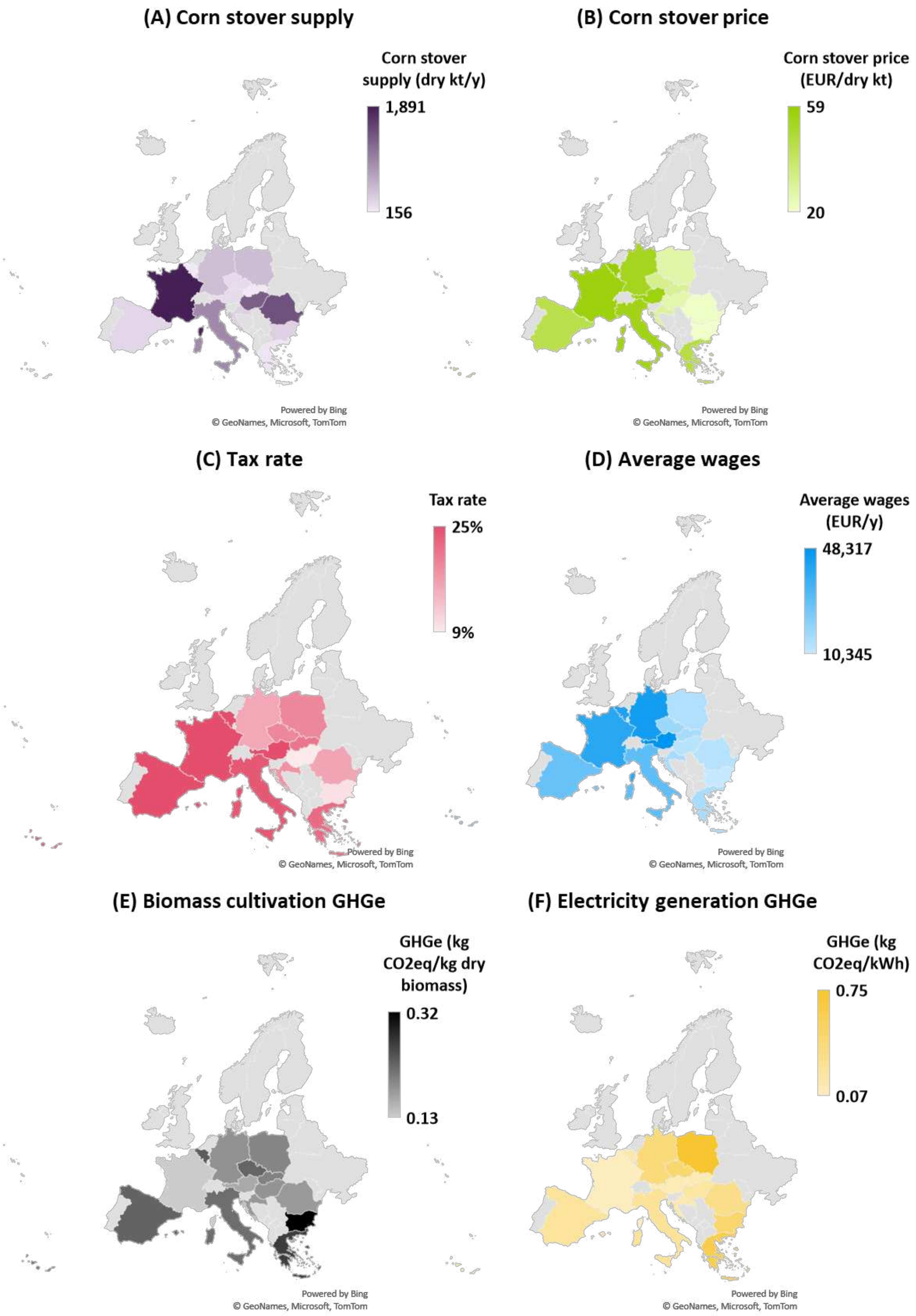

Figure 4. Geospatial variance of (A) corn stover supply, (B) corn stover plant-gate price, (C) tax rate and (D) average salaries, (E) biomass cultivation GHGe and (F) electricity generation GHGe for all case studies.

4. RESULTS AND DISCUSSION

4.1 Base case process simulation results

The major process results are presented in Figure 5 for the four different simulation models. The highest biomass conversion to ethanol was observed for the dilute acid pretreatment model (334 L/dry t), while a 13%, 17% and 35% lower conversion rates were obtained for the steam explosion, liquid hot water and alkaline models respectively. This was expected, as dilute acid pretreatment is the most mature technology and the most reported in literature. On the other hand, the conversions chosen for the rest of the pretreatment methods are based on experimental results. The lower biomass conversion of these methods can also be attributed to the fact that the developed process models do not take into consideration any ethanol production from oligomer sugars. Close to neutral and high pH, sugars tend to stay in their oligomeric and polymeric form [74], which is the case for all pretreatment methods studied except for the dilute acid one.

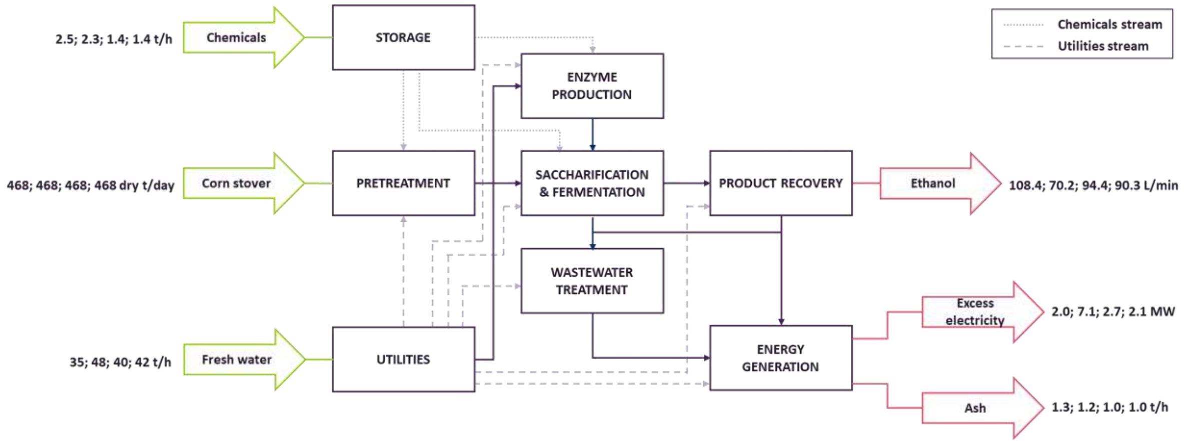

Figure 5. Simplified process flow diagram (PFD) with major mass and energy flows. Stream values refer to dilute acid, alkaline, steam explosion and liquid hot water simulation models respectively.

The chemical pretreatment methods exhibit the highest chemical use. The pretreatment area required 709 kg/h and 600 kg/h of chemicals both for pretreatment and conditioning during dilute acid and alkaline pretreatment respectively. This accounts for around 26-28% of the total chemical consumption of the bioethanol plant. On the contrary, both of the physicochemical pretreatment methods were responsible for only 6.5% of the total chemical consumption. This percentage includes the ammonia used during the conditioning step.

The alkaline and liquid hot water pretreatment methods have the highest water consumption. The cooling water tower system is the main attributor to the high water demand for the alkaline pretreatment model. Alkaline pretreatment is the only method among those evaluated in this study that focuses on the removal of lignin. The simulated bioethanol plant uses lignin as a fuel to a combustor at the energy generation area, which produces steam and electricity through a boiler and a multistage turbine connected with a generator. Steam is generated at two different pressure levels and the remaining is condensed and returned to the boiler system. Due to the high amount of lignin burnt, as well as the lower steam demand because of the low pretreatment temperature, a larger amount of remaining steam is available. In order to condense this steam turbine exhaust, a larger volume of cooling water is required. As far as the liquid hot water pretreatment method is concerned, the use of water as a catalyst in combination with the low solids loading during the pretreatment are the main contributors to the high water consumption. Finally, the excess electricity production was found to be from 2.7 to 3.8 times higher for the alkaline pretreatment model compared to the rest, because of the excess lignin removed during the pretreatment.

4.2 Base case process economics results

Figure 6 summarizes the main economic results of the techno-economic assessment for all simulation models. The CAPEX was the lowest for steam explosion and liquid hot water. These two physicochemical methods require a simpler reactor design, with less expensive materials compared to the chemical pretreatment methods, which create extreme acidic/basic conditions. On the contrary, the alkaline model exhibits the highest CAPEX among all models. This can be explained with the breakdown of the total equipment cost by process areas, as shown in Figure 7 (A).

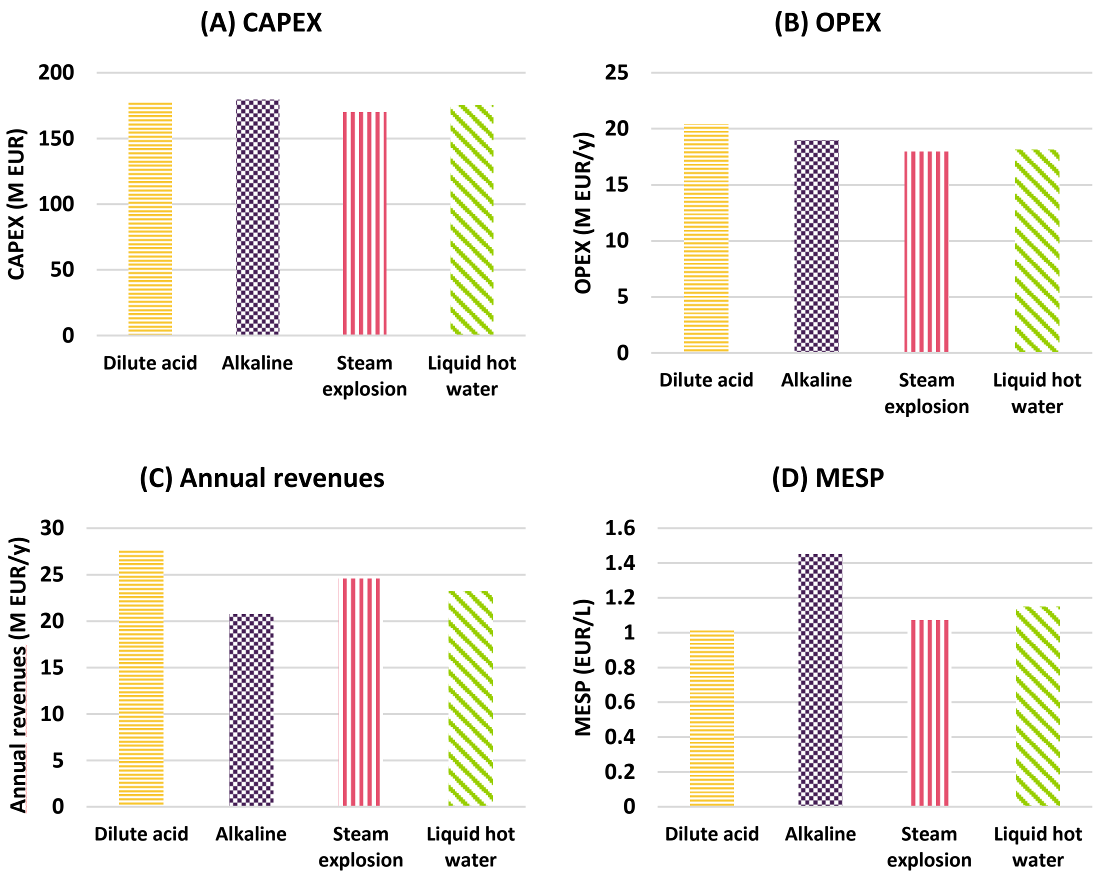

Figure 6. Major techno-economic assessment results for each simulation model: (A) CAPEX; (B) OPEX; (C) Annual revenues; (D) MESP.

The energy generation area has the highest contribution to the total equipment cost for all models, over 30% for all models. The alkaline model requires a larger scale for the energy generation area than the rest of the models, due to its high delignification rate. Overall, pretreatment area accounts for 14%, 13%, 10%, 12% of the total equipment cost for the dilute acid, alkaline, steam explosion and liquid hot water models respectively. The impact of the pretreatment method is responsible for the lowest CAPEX calculated for steam explosion, followed by liquid hot water pretreatment models. The difference between these two physicochemical methods can be attributed to the higher water supply required for the liquid hot water method.

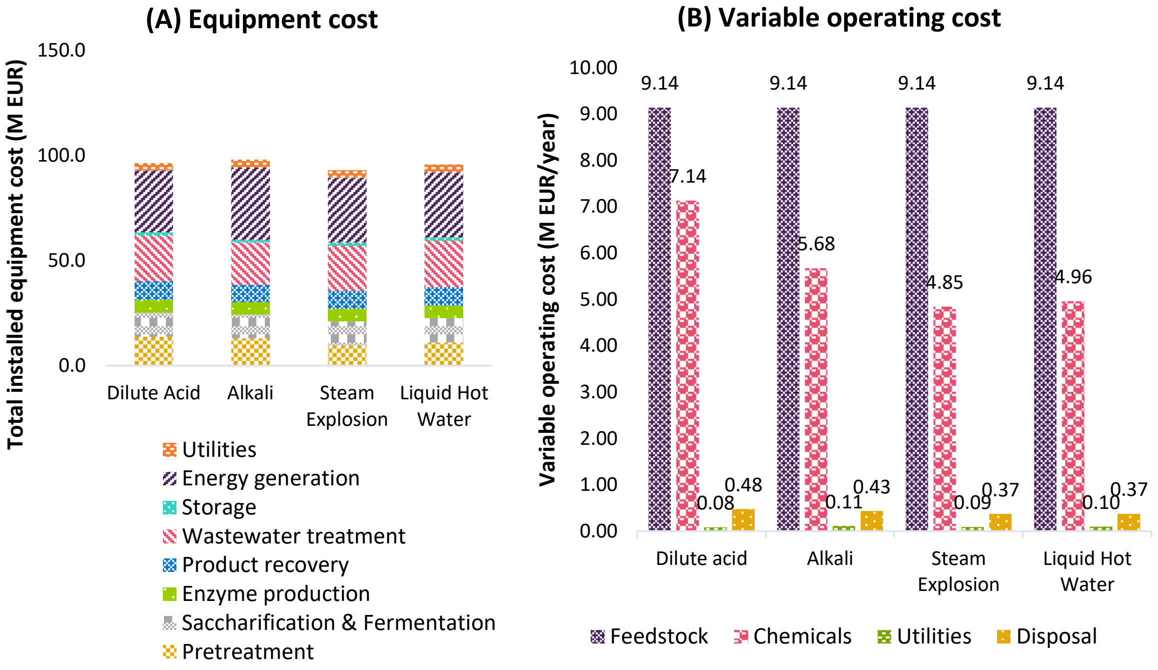

Figure 7. Breakdown of (A) equipment cost and (B) variable operating cost for the four different pretreatment models.

The highest OPEX (Figure 6 (B)) is observed for dilute acid pretreatment model, followed by alkaline, liquid hot water and steam explosion. Feedstock is the major contributor to the variable operating cost, as indicated in Figure 7 (B). Corn stover supply is responsible for 54%, 59%, 63% and 63% of the total variable operating cost for dilute acid, alkaline, steam explosion and liquid hot water pretreatment models respectively. Chemicals cost is the second highest contributor for all models studied. The highest chemicals cost is observed for the chemical pretreatment models, due to the increased need for chemicals during the pretreatment process. Despite the highest price of sodium hydroxide compared to sulfuric acid, dilute acid model has a higher chemicals cost than alkaline model. This can be attributed to the higher acid loading during pretreatment and the higher ethanol production of the dilute acid process model, which requires more chemicals for the downstream processes.

The disposal of the ash collected from the baghouse unit, has the third highest contribution to the variable operating cost for all models. The two chemical methods had the highest disposal cost, due to use of more chemicals, while the physicochemical ones had almost the same. Finally, utilities costs include only the fresh water supply, as steam, electricity, cooling and chilled water are produced on-site. Despite the large amount of fresh water required for the bioethanol plant, it has the lowest impact on the variable operating cost. The highest utilities cost is observed for the alkaline pretreatment, followed by liquid hot water, steam explosion and dilute acid. This is explained by the water consumption required for each method, which was found at 5.41 kg/L, 11.28 kg/L, 7.00 kg/L and 7.67 kg/L of ethanol produced for the dilute acid, alkaline, steam explosion and liquid hot water pretreatment models respectively.

The total revenues of the bioethanol plant include ethanol sales and electricity by-product credit. The ethanol sales are the major contributor, being responsible for around 84% of the total annual revenues for the alkaline pretreatment model and 95 to 96% for the rest. The electricity by-product sales are higher for the alkaline pretreatment model due to the larger amount of electricity produced. The process models with the highest ethanol yield and therefore, ethanol production, were the ones with the highest revenues. Indeed, dilute acid pretreatment model showed the highest annual revenues, followed by steam explosion, liquid hot water and alkaline models (Figure 6 (C)).

The dilute acid pretreatment model has the lowest MESP of 1.01 EUR/L, followed by steam explosion and liquid hot water (Figure 6 (D)). This is attributed to the highest corn stover conversion rate calculated for the dilute acid model, despite having a higher CAPEX and OPEX than the two physicochemical models. Nevertheless, the calculated MESPs are almost 2 to 3 higher than the average ethanol selling price in 2021 market, being 0.51 EUR/L [62]. Similarly, Silva et al. [32] estimated the lowest capital cost for the steam explosion pretreatment simulation model, followed by liquid hot water and dilute acid, but identified dilute acid as the most economically feasible pretreatment method for second-generation ethanol production.

4.3 Base case environmental assessment results

The GHGe for each simulation model were calculated as CO_2 equivalents. The results are plotted against the MESP for each simulation model in Figure 8.The biomass cultivation contribution is the highest for all models, ranging from 60% to 70%. GHGe during ethanol production are higher for the two chemical methods, due to the excess amount of chemicals used. Despite this difference, the lowest GHGe are calculated for the dilute acid model, followed by steam explosion, while the alkaline presents the highest one. This is mainly attributed to the low ethanol yield obtained for the alkaline model, requiring thus a larger amount of corn stover per L ethanol (i.e., the functional unit), which is the main driver for the calculated GHGe. The results are in accordance with Silva et al. [32], who also observed higher GHGe for the steam explosion compared to dilute acid.

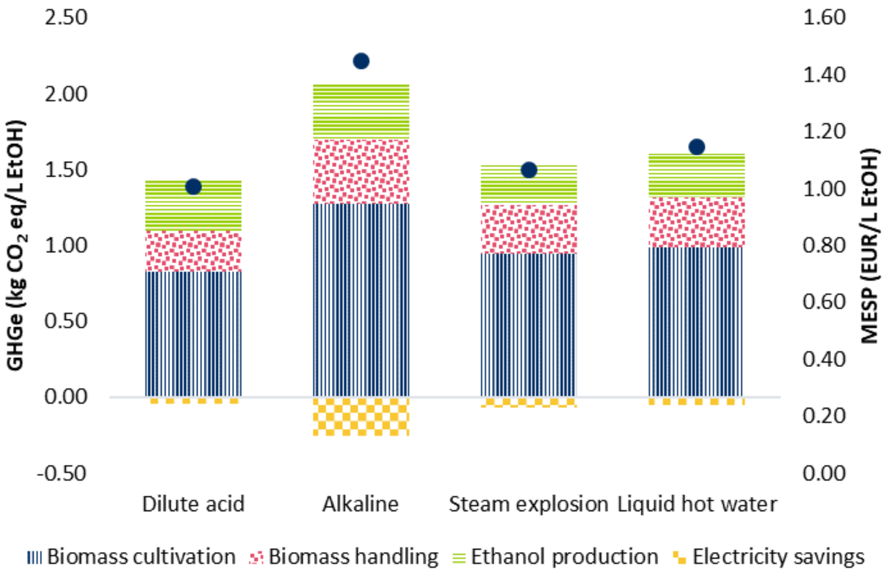

Figure 8. GHGe (stacked columns, primary axis) breakdown and MESP (markers, secondary axis) for each pretreatment technology of the base case study.

In Figure 8, the trade-off between the two main economic and environmental indicators is shown. Dilute acid presents both the best economic and environmental performance, dominating the rest. It is also worth mentioning that the GHGe savings from electricity substitution are significantly high for the alkaline model, which presented the largest electricity production. Therefore, the national electricity mix can have an even higher impact in the calculated GHGe savings from this substitution for countries with a higher carbon intensity in their electricity production.

4.4 Economic Global Sensitivity analysis

Figure 9 illustrates the sensitivity of the MESP under various economic parameters for the different pretreatment methods studied. All variables have a positive correlation with the MESP except for the by-product price. The most influential parameter for all process models is the FCI with more than 50% contribution, followed by the discount rate. This is explained by the high costs associated with the CAPEX, compared to the operational costs. Corn stover cost has also a considerable impact on MESP for all models.

The contribution of the by-product price is significantly higher for the alkaline model, due to the high amount of excess electricity produced compared to the rest of the models. Dilute acid model is also more sensitive to the impact of the chemicals cost. The high chemicals use of this method is the main cause of this contribution. The two physiochemical pretreatment models have a relatively higher impact by the operator wages, which can be attributed to the fact that the OPEX is affected more by the fixed operation cost, due to the low chemicals use.

On the other hand, the two chemical pretreatment models are more sensitive to the biomass cost. The rest of the parameters show no significant difference between the different models.

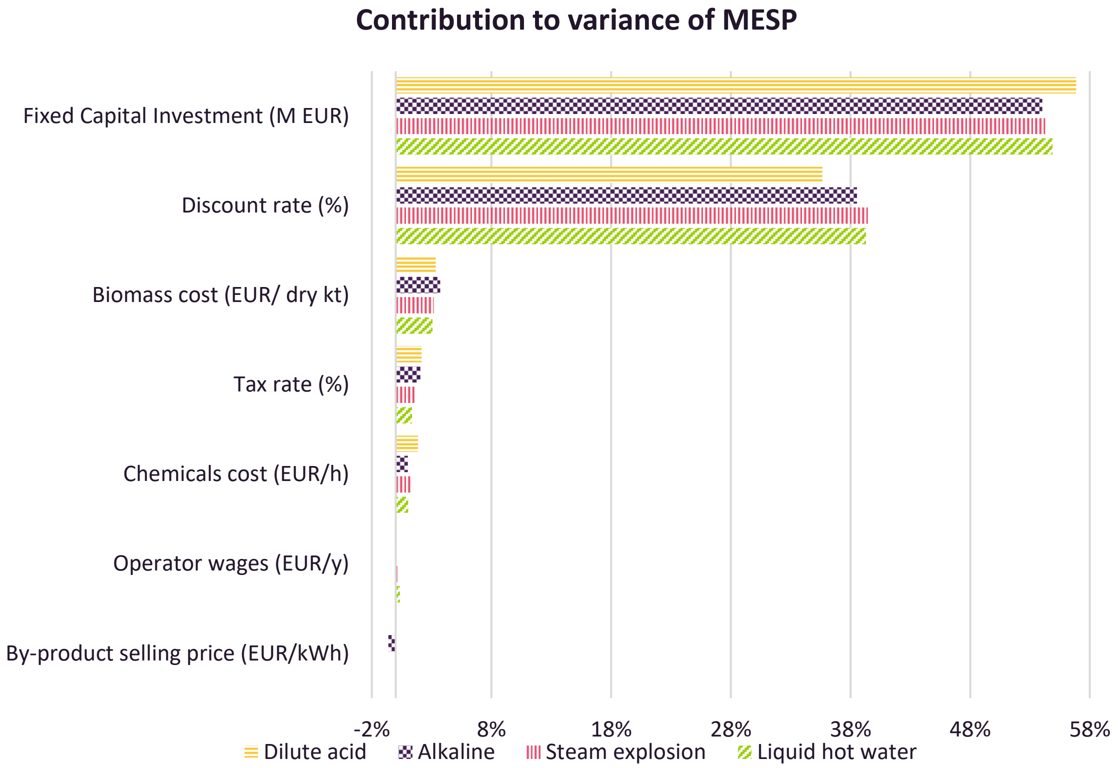

Figure 9. Global sensitivity analysis for four different pretreatment models.

4.5 Geospatial process economic results

The MESP of thirteen countries within the EU, in addition to Belgium (base case) for four different pretreatment technologies, are shown in Figure 10. In all cases, Belgium presents the highest MESP. This can be explained by the fact that Belgian total corn stover production (519 dry kt/y) was used as a minimum threshold, while its tax rate and salaries are among the highest. On the other hand, the lowest MESP (0.39 EUR/L) is obtained for Hungary for the steam explosion model, followed by the liquid hot water one (0.43 EUR/L). Hungary presents the lowest tax rate, the second lowest average salary and the third highest corn stover production between the studied countries. A low MESP (0.43 EUR/L) is also calculated for Romania, by employing the steam explosion pretreatment technology.

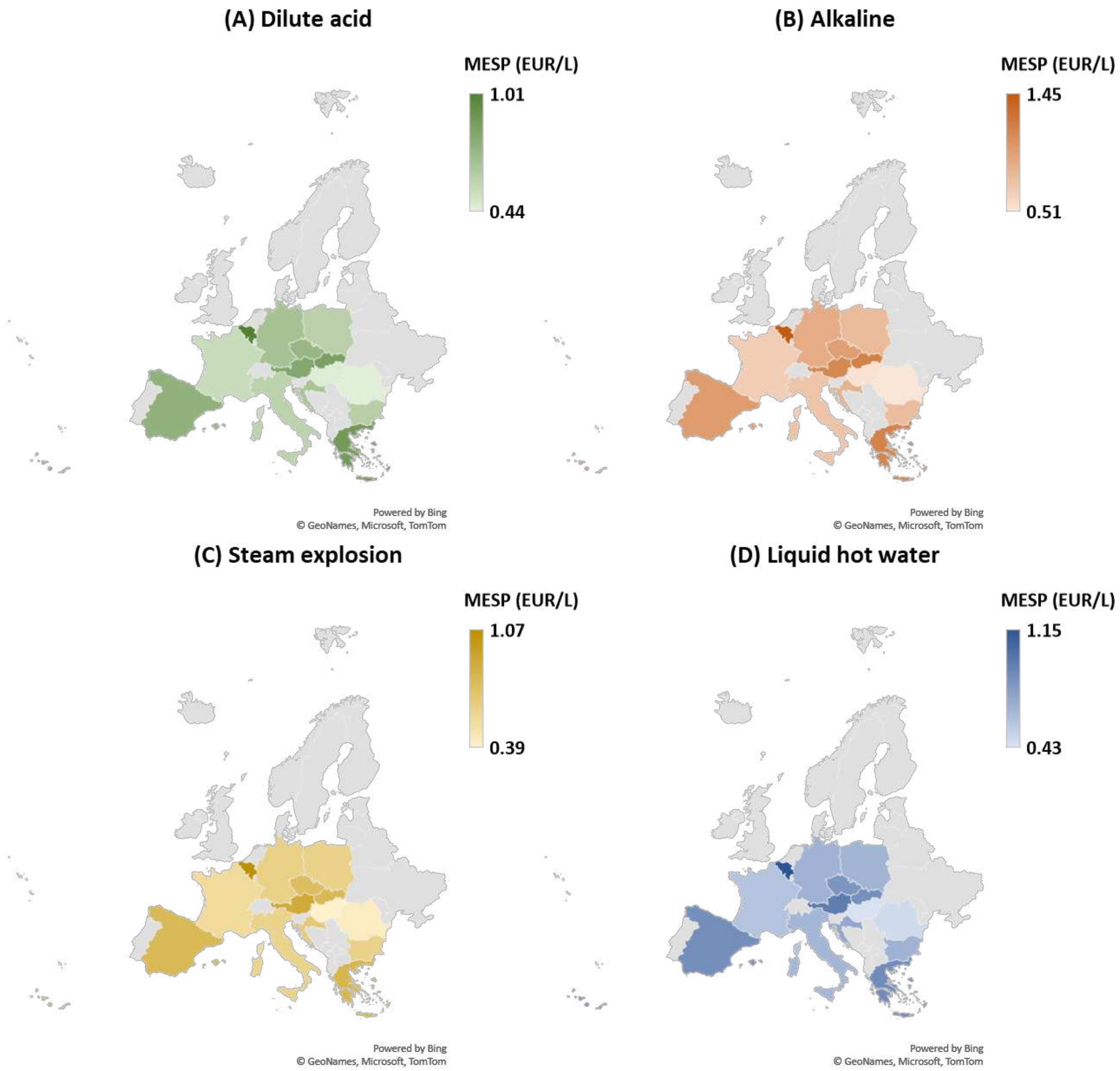

Figure 10. MESP (EUR/L) results for (A) Dilute acid, (B) Alkaline, (C) Steam explosion and (D) Liquid hot water pretreatment models within the EU.

Based on these results, there is a clear location-dependency of the economic performance of different pretreatment technologies. Dilute acid is the most promising technology for nine countries, while steam explosion for five countries. The alkaline model exhibited the worst economic performance for all of the studied countries. The two physicochemical models performed best at Hungary, while the two chemical models at Romania. Indeed, a MESP of 0.44 EUR/L for the dilute acid and 0.51 EUR/L for the alkaline model was calculated for Romania. This can be attributed to the fact that Romania has the second lowest biomass cost among the other countries. The economic performance of the two chemical pretreatment models is affected more by the biomass cost, as indicated by the global sensitivity analysis in Section 4.4. It is worth mentioning that despite Bulgaria having the lowest biomass cost, its performance is worse due to its limited corn stover production.

4.6 Geospatial environmental indicator results

Figure 11 presents the calculated GHGe for four pretreatment technologies in fourteen EU countries (including the base case results). The best environmental performance, indicated by the lowest GHGe, is observed for Poland. This is directly associated with the carbon intensity of Poland's electricity generation sector, which was the highest within the EU during 2021 [72]. In this study, the avoided product allocation is applied for the generated electricity, thus emission savings are significantly higher for countries with a high carbon intensity. GHGe were the highest in Bulgaria, except for the alkaline model which performs worst in Belgium. Bulgaria presents the highest emissions from biomass cultivation practices, which as shown in Figure 8 for the base case, has the biggest contribution to the final calculated emissions. However, when the excess electricity production is higher, then the emissions savings due to product allocation can significantly improve the overall performance, which is the case for the alkaline technology in Bulgaria.

Similarly to the economic assessment results, the environmental performance of the investigated pretreatment technologies is directly connected to the biorefinery location. The lowest environmental impact is obtained for the dilute acid method for eleven countries, while the alkaline technology outperforms the dilute acid in Poland, Germany and Greece. These three countries had the highest carbon intensity in the power sector in EU during 2021 [72]. The alkaline model presents a significantly higher electricity production than the rest of the technologies, which is treated as an avoided product in the performed environmental assessment. The low GHGe of the dilute acid model are associated with its technological performance, as less biomass is required per L of ethanol produced. Therefore, the emissions due to biomass cultivation and handling are lower per functional unit. Finally, France and Germany are the countries with the lowest environmental impact after Poland, due to the low emissions intensity of their cereal production [70].

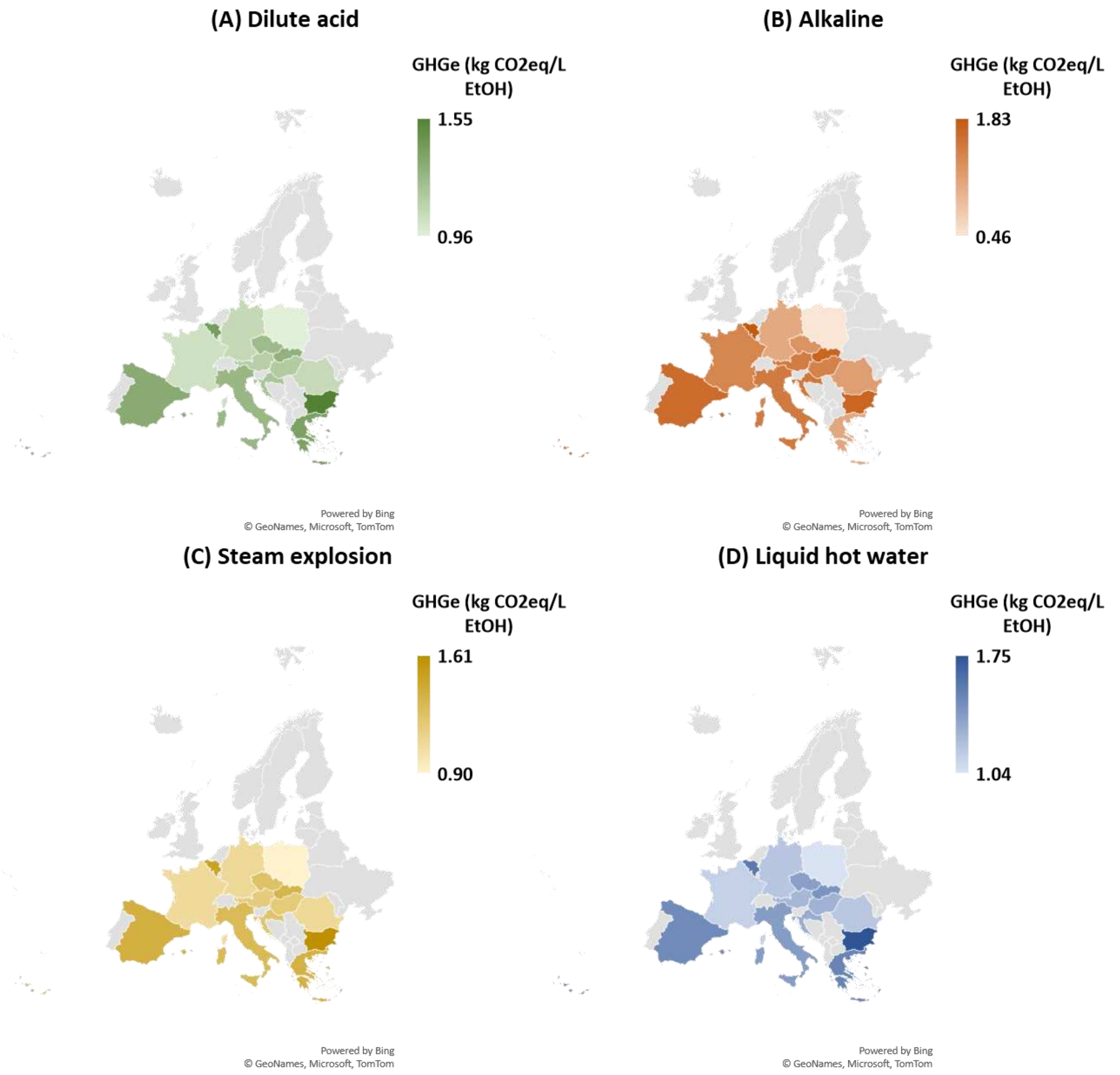

Figure 11. GHGe (kg CO_2eq/L EtOH) results for (A) Dilute acid, (B) Alkaline, (C) Steam explosion and (D) Liquid hot water pretreatment models within the EU.

4.7 Plant capacity break-even point analysis results

The percentage of the plant capacity break-even point to the actual simulated is presented in Figure 12. Hungary and Romania are the only countries with a simulated plant capacity higher than the break-even point. Indeed, a 40-60% of the simulated plant capacity is required to reach a net present value of zero for the steam explosion, liquid hot water and dilute acid models. The break-even point for the alkaline model is almost the same as the simulated supply, for the two countries. Given the assumptions made for the corn stover that is available for biofuels production and is supplied to only one biorefinery, a high potential for these two countries is identified.

A two to four times higher biomass supply is required for six countries, namely Bulgaria, Croatia, France, Germany, Italy and Poland. Given the restricted corn stover availability in these countries, such a large plant capacity is not feasible. However, mixed feedstock supply could be an alternative option to tackle the biomass availability limitations. Simultaneous processing of different lignocellulosic biomass has been investigated in literature. Nielsen et al. [75] calculated an ethanol yield of 74-78%, by performing acid-catalyzed steam pretreatment on a mixed feedstock of corn stover and wheat straw. Shi et al [76] performed saccharification on an ionic liquid pretreated feedstock mixture and estimated a 90% sugar yield. Therefore, the use of different lignocellulosic feedstocks in the same biorefinery could increase the plant capacity and potentially improve its economic performance.

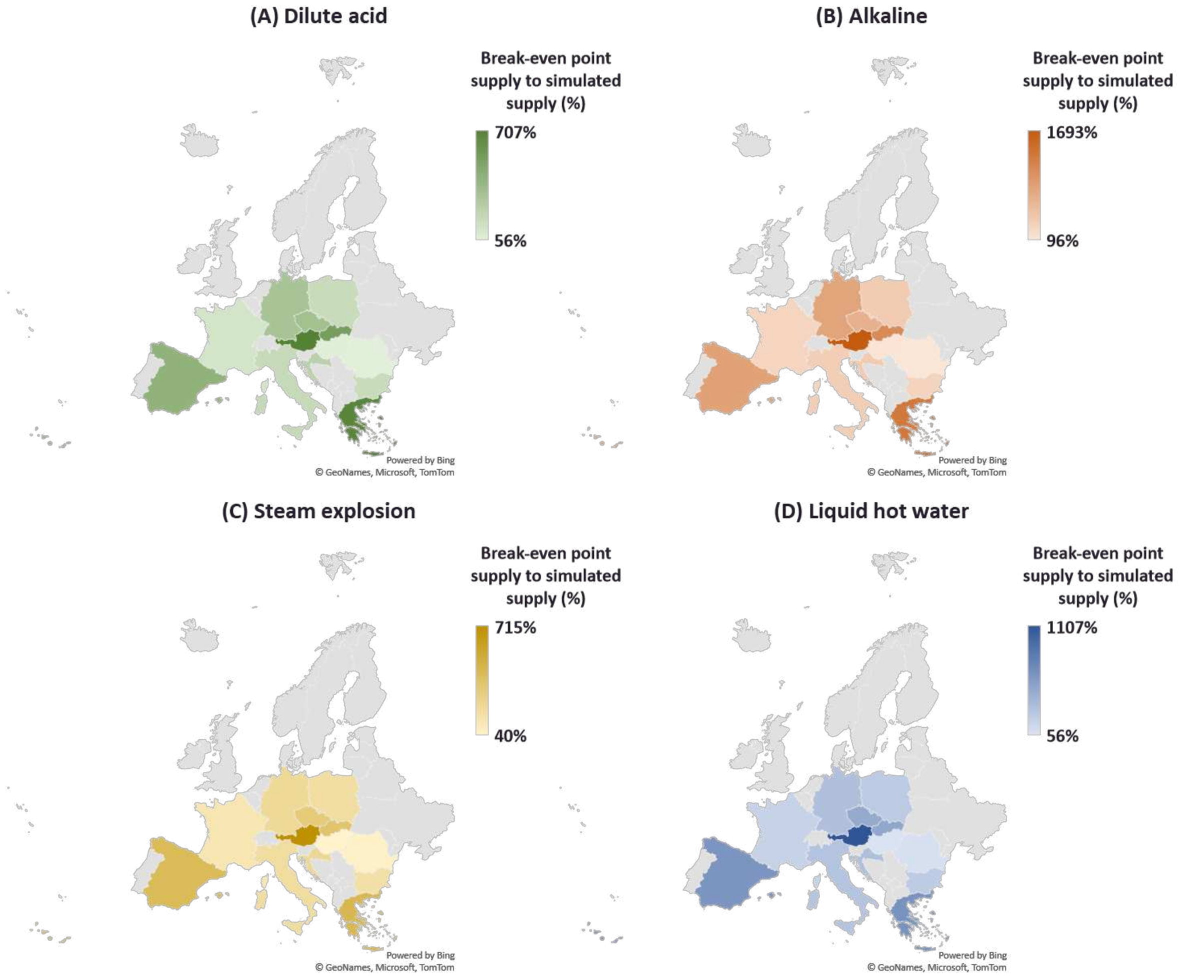

Figure 12. Plant capacity break-even point to simulated plant capacity (expressed in %) for different biorefinery locations within the EU for (A) Dilute acid, (B) Alkaline, (C) Steam explosion and (D) Liquid hot water models. Belgium is excluded from the graph due to the relatively high difference with the rest of the countries.

4.8 Discussion

The ETEA performed in this study aims to evaluate the performance of second-generation ethanol production from corn stover in the EU, deploying different pretreatment technologies. The base case study in Belgium indicated a poor economic prospective of second-generation bioethanol from corn stover in the country. Therefore, due to feedstock availability limitations in Belgium, the potential to improve the economic feasibility of second-generation ethanol is linked to the key parameters identified by the global sensitivity analysis. The FCI and discount rate were the two major parameters with the highest influence on the MESP. These factors are directly connected with the chosen processes and their maturity. Finally, by taking into consideration both the economic and environmental performance of each pretreatment model, the dilute acid and steam explosion technologies showed the highest potential for the base case study. Emissions during biomass cultivation had the highest contribution to the final GHGe indicator, while the carbon intensity of the electricity generation sector had also a significant effect due to the applied avoided product allocation.

However, these results are location-dependent, indicative only for the base case study. This was validated by geospatially varying key parameters within thirteen more EU countries. Indeed, different results were obtained for both the economic and environmental performance, when taking into consideration different biorefinery locations within the EU. The lowest MESP was observed for Eastern European countries. Both Hungary and Romania have the second and third lowest biomass cost and tax rate, their average wage is less than 13000 EUR/y while their corn stover production is among the highest. Those parameters were sufficient enough to provide a MESP lower than the average ethanol selling price in the EU, making a second-generation bioethanol production plant economically viable. The poor economic performance of few investigated countries indicates the effort required to make this bioethanol plant economically feasible, under the assumptions made in this study. Also, the plant capacity break-even point analysis indicated the importance of the biomass availability, which is limited in most of the economically poor performing countries. More research towards the pretreatment processes or different biomass valorization pathways, could potentially make this biorefinery viable.

The lowest GHGe were obtained for Poland, Greece, France and Germany. The high carbon intensity of the electricity generation sector of Poland and Greece and the low emission intensity of the French and German cereal agriculture sector were the main drivers of the obtained results. Dilute acid model showed the best environmental performance in almost all case studies, but, notably, the alkaline pretreatment technology showed a better performance in three countries, those being Poland, Germany and Greece.

Therefore, a location dependency of each pretreatment technology was identified, as both the economic and environmental performance varied significantly between the investigated case studies. Multiple technology variances for a specific case study should be taken into consideration, as a different performance can be obtained. This can have a significant impact on the final optimal technology choice when stakeholders are investigating potential investments. Moreover, the geospatial variance of major parameters should be considered by researchers when investigating novel technologies, as their performance can vary based on the studied location. The obtained results of the current study can also be valorized by policymakers within the EU to identify the barriers and the drivers of each pretreatment technology application. Finally, the framework applied in this study can be extrapolated to other large regions, such as the USA, East Asia, Africa etc., as the identified technology performance differences within the EU are very likely to exist in other regions around the world.

4.9 Limitations & Future work

The alkaline pretreatment emerges as the worst in terms of economic viability for all case studies. This technology has a high biomass delignification rate, resulting in a large amount of lignin being further valorized towards steam and electricity. However, lignin could also be valorized differently, as there is an increasing interest in lignin-first biorefineries aiming at producing high added-value chemicals [77,78], which can improve the economic viability as co-products to bioethanol in an integrated biorefinery concept starting from lignocellulosic biomass. Therefore, different co-products in combination with bioethanol can be investigated in future work, as they can have a significant impact in the biorefinery performance.

The EU's Emission Trading System allows participating installations to trade CO_2 allowances [79]. The current system does not cover biorefineries, while the very recently revised EU ETS II, which is set to be implemented in 2027, will cover more sectors such as fuel distribution for road transport and buildings [80]. Due to the policy uncertainties, extremely volatile carbon prices (notably European Emission Allowance prices ranged from 24 to over 100 EUR/t CO_2 from 2020 until 2023 [81]), as well as the fact that the main product of the investigated biorefinery is bioethanol, which is currently used as blended fuel within the EU and does not substitute an already existing fossil-based fuel, the possible CO_2 credits were not included in the economic assessment.

The avoided product allocation approach applied in this study has a significant effect on the environmental performance of the investigated technologies. Since electricity is sold as a by-product to the national grid, the system expansion allocation method was chosen, gaining emissions savings from substituting this electricity in the national electricity mix. The environmental performance results are thus subjected to the assumptions made during the environmental assessment.

During the geospatial scenarios of different case studies, only few major parameters were taken into consideration. In particular, the equipment costs are assumed to be the same for all case studies. A location factor could be applied, in order to capture the difference of building a plant in different countries. However, due to the lack of data on recently available location factors for all of the investigated countries, as well as the criticism over the use of location factors due to globalization (most installation factors are close to 1.0) [52], this was not included in the study.

As far as the environmental performance is concerned, only the biomass cultivation and electricity mix are varied. In particular, aggregated data on emissions from cereals cultivation are used, which include corn, barley, oats, rye, wheat and sorghum. It is thus possible that an under- or over-estimation of the GHGe from corn cultivation is made. A recently published review on LCA studies in biorefinery systems, revealed the importance of spatiotemporal LCAs [82]. Therefore, the application of a complete geospatial LCA could improve the findings of this study, providing more accurate results on the environmental performance of a technology for a specific location. In addition to the geospatial variance, taking into consideration also the temporal could improve further the obtained results, which are currently affected by both the biomass cultivation practices and the electricity mix of the investigated countries, which are expected to significantly change over the next years, in order to meet the EU's climate neutrality target [13]. It is thus evident that the underlying assumptions have a significant positive or negative influence on the environmental performance and should be taken into consideration by the relevant bodies.

Finally, all values used in the current study are fixed and based on the available literature. A global sensitivity analysis has been conducted for the economic parameters, indicating the influence of key parameters. Also, given the importance of the biorefinery scale, a plant capacity break-even point analysis was conducted to identify the required biomass needed. However, a complete uncertainty analysis on both economic and environmental parameters could identify and quantify the effect of potential errors in the input data used.

5. CONCLUSION

An environmental techno-economic assessment was conducted to identify the most promising pretreatment technology for a second-generation ethanol production plant in EU, using corn stover as feedstock. Dilute acid, alkaline, steam explosion and liquid hot water methods were simulated in ASPEN Plus and their economic and environmental performances were firstly evaluated for a base case study in Belgium. Based on the obtained results, major influential parameters were identified and varied within the EU. The lowest MESP was obtained for Hungary at 0.39 EUR/L and for Romania at 0.43 EUR/L for the steam explosion technology. This is mainly attributed to the low biomass cost, tax rate, salaries and the high corn stover production of Eastern European countries. Poland presented significantly lower GHGe than the rest of the case studies, at 0.46 kg CO_2eq/L EtOH, due to the avoided product allocation applied for the electricity by-product and its extremely high electricity generation carbon intensity during 2021. Low GHGe were also obtained for France and Germany, where low emissions by the cereal agricultural sector are observed. The geospatial ETEA framework applied in this study indicated a location relationship between both the economic and environmental performance and pretreatment technologies. Therefore, the investigated parameters should be taken into account when assessing the performance of pretreatment technologies, while a complete spatiotemporal LCA could further improve the accuracy of the obtained results.

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