

Technoeconomic assessment of potential processes for bio-Ethylene production

Abstract

The use of biomass in the production of plastics can contribute to the depletion of greenhouse gas (GHG) emissions and secondarily to partially fulfill the growing demand for plastics expected in the near future. The aim of this study is to assess the production of ethylene, one of the most important commodities in the petrochemical industry, via the dehydration of bioethanol and the conversion of bio-dimethyl ether (bio-DME) into olefins. Four case studies have been developed taking into account the different origins of bioethanol, and one for the conversion of bio-DME. The assessment includes current and promising processes for the production of bioethanol, i.e., 1st generation and 2nd generation bioethanol. The latter comprises biochemical processing (enzymatic hydrolysis), thermochemical processing (both direct and indirect syntheses from syngas) and hybrid processing (fermentation of syngas) of biomass. The results show that two of the considered case studies (Brazilian ethanol and ethanol via indirect synthesis from syngas) enable the cost-competitive production of ethylene at current market prices. If BECCS (Bioenergy with Carbon Capture and Storage) is taken into account for the case studies, the results would be substantially enhanced and all cases, except for the case of bioethanol from biochemical processing, would be profitable.

Keywords: Ethylene; Biomass; 1st generation bioethanol; 2nd generation bioethanol; Thermochemical processing; Technoeconomic assessment

1. Introduction

The production of plastics from a renewable feedstock is of great interest nowadays. The use of biomass and carbon-based waste in the production of plastics can contribute to the depletion of greenhouse gas (GHG) emissions and secondarily to partially fulfill the growing demand for plastics expected in the near future. There are several renewable feedstocks for plastic production [1], but only a limited number of petrochemical commodities could be produced from biomass using commercial or potential commercial technologies. These commodities are ethylene, propylene and BTX (benzene, toluene and xylenes) [1], which can be easily introduced in current petrochemical facilities. However, regarding both the plastic market and processing of biomass, bio-ethylene seems a reasonable medium-term target. Two reasons support this position: first, ethylene is by far the largest-volume commodity of the three mentioned above; and second, it can be produced by available or demonstrated technologies, such as the dehydration of ethanol or methanol(DME)-to-olefins [2]. Currently, the main use of ethylene is the production of plastics (via polyethylene or vinyl acetate) [2].

Nomenclature	
BECSS:	bioenergy with carbon capture and storage
BETE:	bioethanol-to-ethylene
BTL:	biomass-to-liquid
BTX:	benzene, toluene and xylenes
CCS:	carbon capture and storage
DME:	dimethyl ether
GHG:	greenhouse gas
HHV:	high heating value
IEA:	International Energy Agency
LPG:	liquefied petroleum gas
RKS–BM:	Redlich–Kwong–Soave with Boston–Mathias modifications
WWT:	waste water treatment

The price of ethylene is being highly dependent on the price of crude oil (see Figure 1), since half the price of ethylene is due to the feedstock (crude oil) cost [2]. Hence, the production costs of plastics, which in general use petrochemical commodities like ethylene as source, are related to the evolution of crude oil price and therefore suffer from its volatility. The introduction of biomass as a secondary or alternative feedstock would have two positive effects from an economic point of view. On the one hand, it would reduce the dependence on crude oil prices, whose evolution has fluctuated dramatically in recent years. On the other hand, it would improve industrial development in regions without natural fossil sources, but with a relatively high capacity for biomass production.

From a sustainable point of view, the potential of GHG reductions inherent in the use of biomass as a renewable carbon feedstock can be enhanced by using carbon capture and storage (CCS). This option has been recently proposed by the International Energy Agency under the BECCS (Bioenergy with Carbon Capture and Storage) concept [3]. The storage of CO₂ with a renewable or *green* origin allows for the possibility of selling the amount of CO₂ sequestered via CO₂ credits (emissions trading).

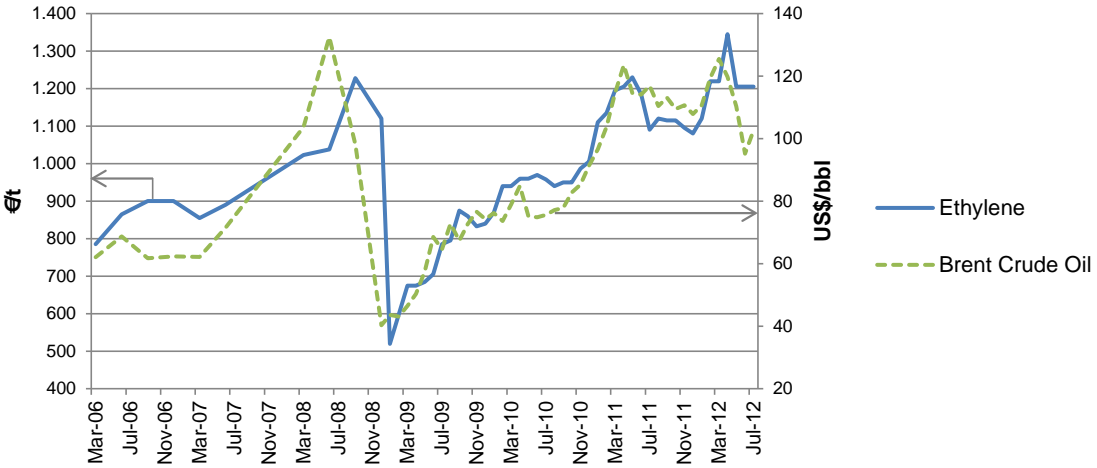


Figure 1. Ethylene contract bulk price and Brent Crude Oil price evolution from 2006 to 2012 (data taken from [4, 5]).

The aim of this work is to study the technical and economic feasibility of different alternatives to produce bio-ethylene from biomass and to assess the possibility of extra revenues with the integration of BECCS into the processes. To date there is no published work in the literature focused on the study of bio-ethylene production and the comparison of different alternatives. Another contribution of this study is the consideration of BECCS and the possibility of extra revenues from CO₂ emissions trading.

The considered alternatives for the production of bio-ethylene are shown in Table 1 and Figure 2, and represent the current most promising routes for ethylene production from biomass. In the first set of alternatives, ethanol is the selected platform chemical for the production of ethylene (via dehydration). As ethanol can be produced from biomass by using different processes, the most representative and innovative have been included, i.e. 1st generation bioethanol, 2nd generation bioethanol via enzymatic hydrolysis and syngas fermentation, and 2nd generation bioethanol via thermochemical processing. In the case of bioethanol via thermochemical processing, both the conventional syngas processing (direct route) [6] and also an innovative process recently assessed (indirect route) with promising results [7] are included. In the second set, ethylene is produced along with other olefins, mainly propylene, using DME as the platform chemical. In this process, DME is catalytically converted into hydrocarbons and it has been recently evaluated in a previous study [8].

2. Description of the case studies

This section provides an outline of the five case studies (see Table 1 and Figure 2), including a summary of the technology involved, process design and system boundaries for the modeling. The section is divided into two blocks accounting for alternatives using ethanol as a platform chemical and that using DME.

2.1. Case studies involving ethanol dehydration (case studies 1-4)

In case studies 1-4 the ethanol input for the dehydration plant is assumed to be commercial fuel grade or anhydrous ethanol. Hence, ethanol processing is the same regardless of the considered case study. For case studies 1 and 2, the plant capacity is not restricted and they are assessed for a range of plant capacities. For case studies 3 and 4 the production of ethylene is assumed to be integrated with ethanol synthesis using the process designs of the previous studies. Hence, the plant capacity in these cases is fixed. Possible alternatives for the modeling of case studies 1-4 are given in section 5.1.

2.1.1. Case study 1: 1st generation ethanol

Despite the controversy surrounding the use of food-competitive feedstock, there is a great interest in the valorization of 1st generation ethanol to high-value products. Production of ethylene was one of the first examples, e.g. the BETE (BioEthanol-To-Ethylene) process in the 1980s [12]. The relatively low-cost of 1st generation ethanol in Brazil [9], along with the

increasing price of crude oil, triggered the interest in the use of ethanol as a platform chemical [2, 13].

Despite 1st generation ethanol representing an appealing option for ethylene production, the optimal capacity of the dehydration plant is still uncertain. Typical sizes of new ethanol plants are about 300–500 ML/year [9], whereas the average size of an ethanol plant in Brazil is about 50 ML/year [2]. This wide range of plant capacities leads to an equivalent range of ethylene production capacities if a *one-to-one* strategy is followed, i.e. the dehydration plant is fed with the production of a single ethanol plant. However, Braskem S.A. has recently put a combined dehydration-polymerization plant into operation with a capacity of 200 tonnes/year of polyethylene and ethanol consumption of 462 ML/year [14]. The size of Braskem's plant suggests that the *one-to-one* strategy is inappropriate. The selected capacities used in this assessment range from 150 to 500 ML/year (118–395 tonnes/year) of ethanol. In this study, we consider the most relevant sources for commercial ethanol, i.e. EU, USA and Brazil.

Table 1. Summary of studied cases for ethylene production from biomass.

Case study	Technology	Platform chemical	Status	Reference
1		1 st generation ethanol	Already commercial	Comercial bioethanol from EU, USA and Brazil [9]
2	Dehydration	2 nd generation biochemical ethanol (enzymatic hydrolysis) & ethanol via syngas fermentation	Close to commercial introduction	Kazi et al. [10] Fornell et al. [11]
3		2 nd generation ethanol (thermochemical, direct route)	In advanced stage of development	Villanueva et al. [6]
4		2 nd generation ethanol (thermochemical, indirect route)	In a first stage of development	Haro et al. [7]
5	MTO	DME	Close to commercial introduction or already commercial	Haro et al. [8]

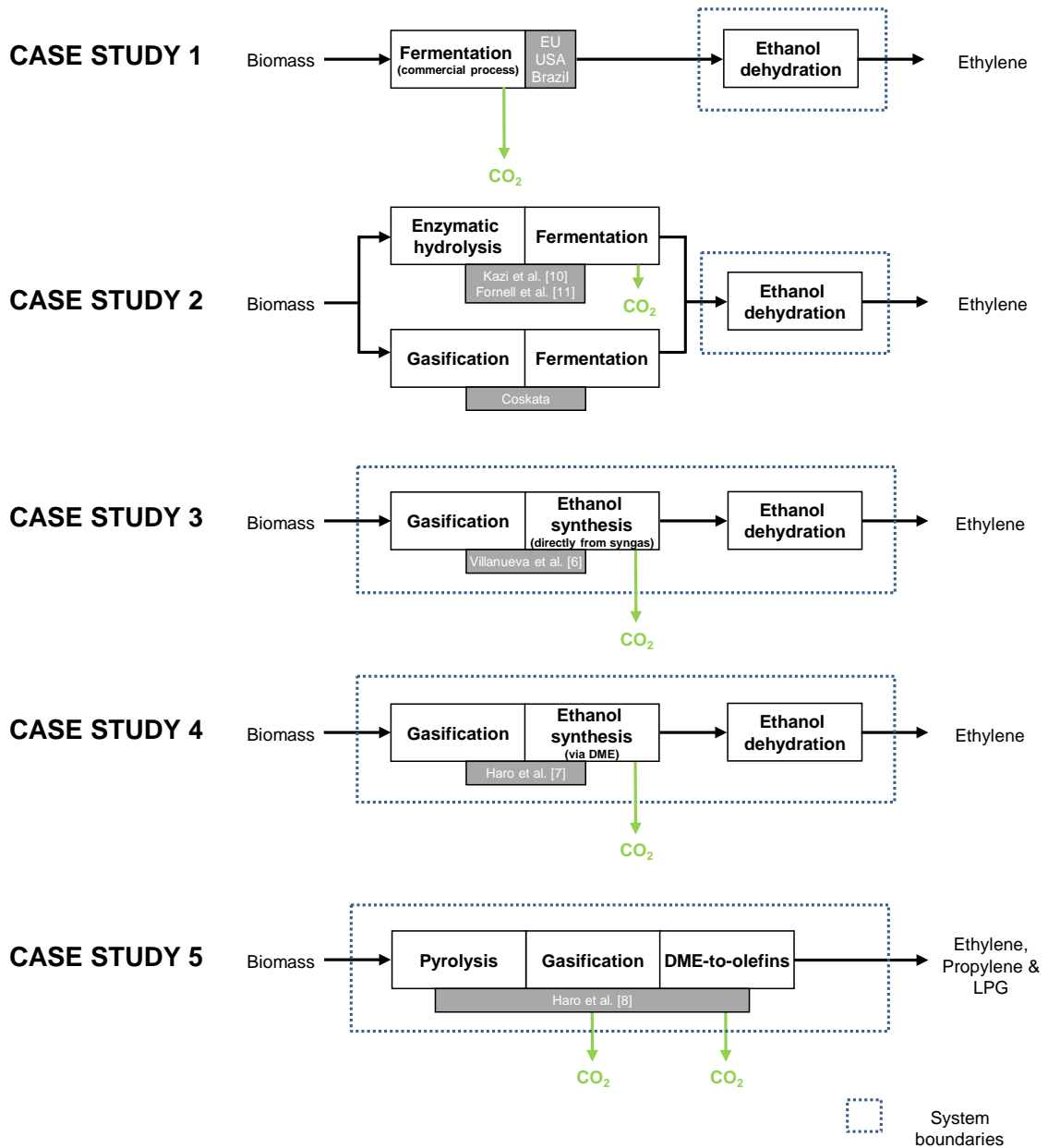


Figure 2. Outline of selected case studies and system boundaries used in this assessment.

2.1.2. Case study 2: 2nd generation ethanol via enzymatic hydrolysis and via syngas fermentation

Although 2nd generation ethanol is in an advanced stage of development, there are no commercial plants in operation, so the impact on the bioethanol commercial trading price is unknown. In this study, the only estimation of prices (production cost) has been collected from literature. Nonetheless, 2nd generation ethanol needs to be included in this assessment as it represents the most likely short-term alternative for current bioethanol production. Three alternatives are in development within 2nd generation processes: biochemical processing (via enzymatic hydrolysis), bio-thermochemical processing (via syngas fermentation) and thermochemical processing (discussed in case studies 3 and 4). Advantages and detailed discussions on current research for 2nd generation bioethanol, e.g. projects, pilot plants and techno-economic assessments, are given in [15-24]. The fermentation of biomass-derived syngas into ethanol is an extremely interesting alternative to conventional production processes and it is or has been in development by some companies, e.g. Coskata and LanzaTech. In spite of the interest in syngas fermentation, there is a lack of public information on the resulting ethanol price.

The plant size for a dehydration plant based on 2nd generation ethanol is subject to more uncertainties than in case study 1 (using current bioethanol). If a scenario of complete introduction of 2nd generation processes is selected, the ethanol production capacity of 2nd generation processes could be twice or three times greater than the largest ethanol plants (assumption by the authors). Therefore, the selected capacities in the assessment range from 300 to 1000 ML/year (236–790 tonnes/year) of ethanol.

In order to perform this technoeconomic assessment two previous assessments of 2nd generation ethanol via enzymatic hydrolysis have been selected as references, i.e. from the Chalmers University of Technology [11] and from the National Renewable Energy Laboratory (NREL) [10]. For the assessment of 2nd generation ethanol via syngas fermentation, we have assumed an ethanol price according to the latest public information from Coskata Inc. [25]. However, recent news from Coskata says that they have withdrawn their plans to use biomass and they are currently focusing on natural gas [26].

2.1.3. Case study 3: 2nd generation ethanol via thermochemical processing (direct route)

The production of bioethanol via thermochemical biomass processing involves the gasification of biomass and further conversion of syngas into ethanol. This conversion can be conducted directly, i.e. in a single catalytic reaction step, or indirectly. The direct conversion of syngas into ethanol and higher alcohols has been of great interest in the field of biomass-to-liquids (BTL) research [6, 27-35].

In this study, the techno-economic assessment of Villanueva et al. [6] has been selected as a reference. The plant capacity is 2140 dry tonnes/day of wood chip (500 MW_{th}). The production of ethanol and higher alcohols is carried out via pyrolysis and entrained flow gasification and subsequent synthesis using a Rh- or a MoS₂-based catalyst. The bases for the conversion of syngas into ethanol and higher alcohols are summarized in Table 2. Figure 3 shows the flowchart of the process. In this study, only the alternative using MoS₂-based catalyst (a proprietary catalyst) is analyzed [6].

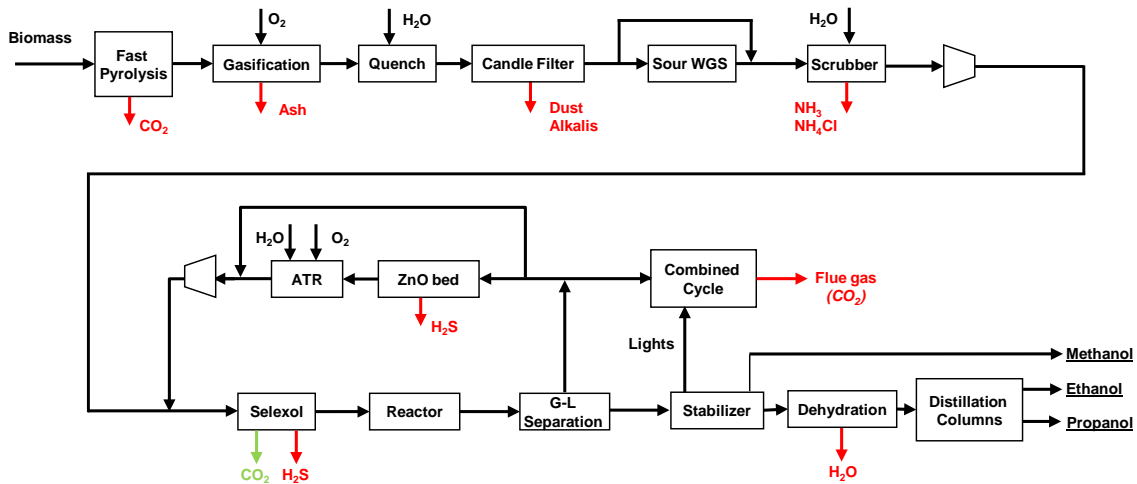


Figure 3. Process flowchart of the thermochemical production of ethanol and higher alcohols via direct synthesis (adapted from [6]).

Table 2. Process conditions for the direct synthesis of ethanol from syngas (MoS₂ Abengoa Bioenergy catalyst) [6].

Temperature (K)	573
Pressure (MPa)	9.0
CO conversion (%)	35.3
H ₂ /CO molar ratio	1.0
Selectivity to product (% molar)	
Ethanol	35.4
Methanol	7.5
Propanol	4.2
Light gas	17.7
CO ₂	35.2

2.1.4. Case study 4: 2nd generation ethanol via thermochemical processing (indirect route)

The direct synthesis of ethanol from syngas suffers from important limitations e.g. low selectivity, which reduces the efficiency of the ethanol production [27, 36]. Hence, the indirect synthesis via DME hydrocarbonylation has been proposed to produce ethanol from syngas with better efficiency as well as economics [7, 27, 37]. However, the indirect synthesis of ethanol

from syngas is in a preliminary stage of development, therefore the DME hydrocarbonylation route is included in this study only as a potential long-term alternative.

The bases for the conversion of syngas into ethanol via DME hydrocarbonylation are summarized in Table 3 and the corresponding process flowchart is illustrated in Figure 4. In this study, only the best case of the previous assessment (i.e. CO/DME molar ratio 10:1) is included, which uses a combination of Cu-ZnO and H-Mordenite catalyst in a dual catalytic fixed-bed reactor [7].

2.1.5. Ethanol dehydration to ethylene

The dehydration of ethanol (Eq. (1)) is an established technology commercially available for the production of ethylene [2, 38-42]. In this study, the design of the dehydration process is based on commercial technology [43]. Table 4 shows the reaction conditions used for the modeling of the dehydration reactor applicable to case studies 1-4.



Figure 5 presents the process flowchart for the ethanol dehydration plant. The ethanol feedstock is mixed with water in a 1:1 molar ratio, pumped and preheated before entering the dehydration reactor. The outlet stream from the dehydration reactor is cooled and compressed for dewatering and conditioned for the recovery of ethylene. The gas stream requires only two fractionation columns, i.e. a first column for C₃- and C₄₊ hydrocarbon splitting, and a second one for the removal of ethane and propylene. The final product stream contains 99.99% (on a weight basis) ethylene with methane as the main impurity. Recovered hydrocarbons are fed to a gas combustor for thermal integration of the plant, although additional natural gas is required to satisfy the power integration of the plant.

2.2. DME-to-olefins (case study 5)

In this case study, DME instead of ethanol is used as the platform chemical for ethylene synthesis. The process has been modeled according to the bioliq[®] concept, which is currently being developed at the Karlsruhe Institute of Technology (KIT) and focuses on the conversion of low-grade lignocellulosic biomass, such as residual wood or straw, to synthetic fuels and other organic chemicals [44-46], as presented in Figure 6. The production of olefins (ethylene and propylene) from syngas via DME was previously modeled and assessed based on a large scale realization of the bioliq[®] concept in Germany [8]. Modeling of previous processing stages (i.e. pyrolysis step, production of syngas by entrained flow gasification and syngas cleaning and conditioning) are described in [47, 48].

The process conditions bases for the conversion of syngas via DME into ethylene, propylene and LPG (light gas and butenes) are summarized in Table 5 and the process flowchart is shown

in Figure 7. In this study, only the best case of the previous assessment is considered [8]. Compared to case studies 1-4, in this case, propylene and LPG are co-produced. The biomass input is larger than in case studies 3 and 4 (see Figure 6).

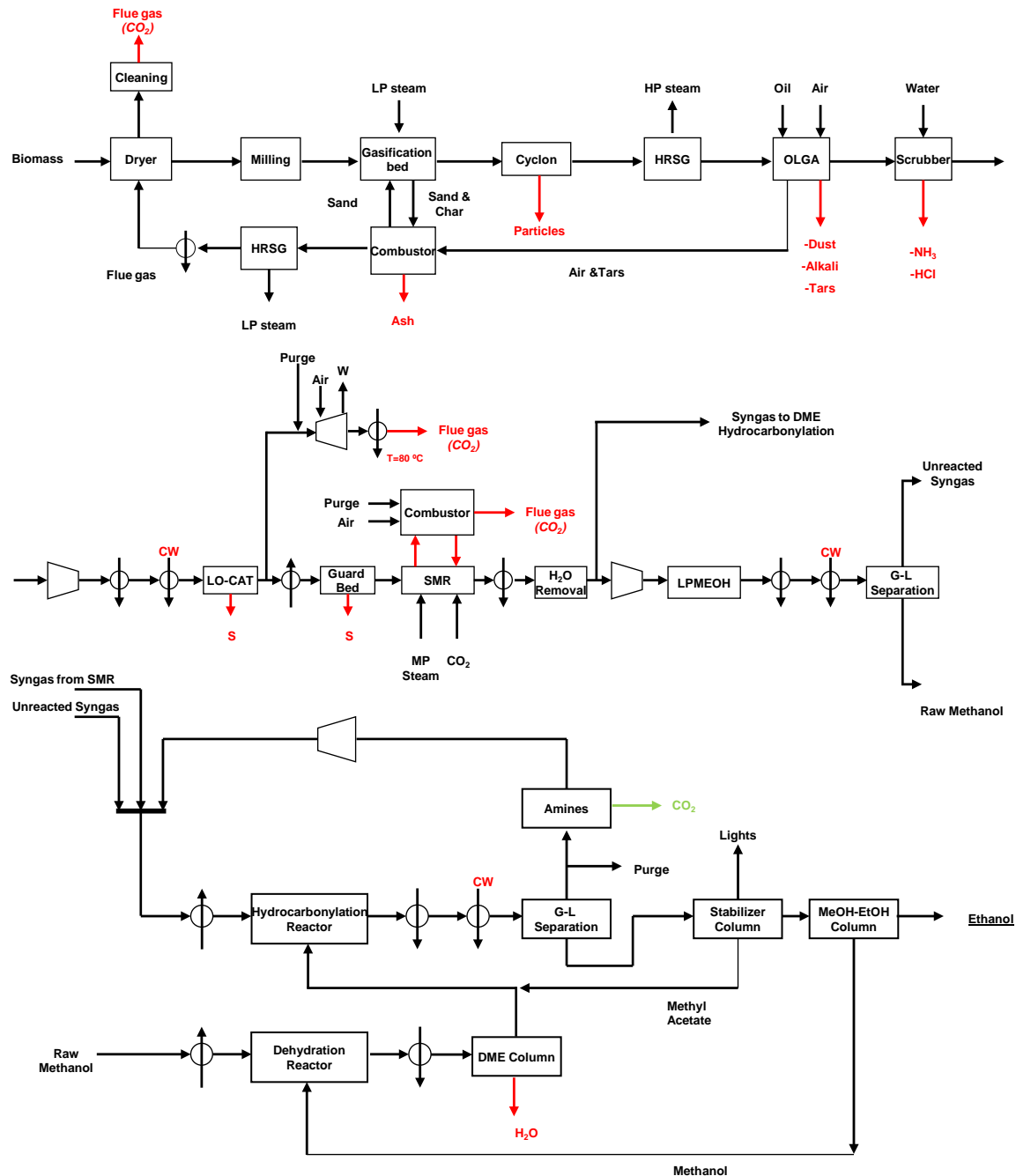


Figure 4. Process flowchart of the thermochemical production of ethanol via indirect synthesis (adapted from [7]).

Table 3. Process conditions for the indirect synthesis of ethanol from syngas via DME hydrocarbonylation [7].

Methanol synthesis	Temperature (K)		523	
	Pressure (MPa)		4.9	
	CO conversion (%)		31	
	CO ₂ conversion (%)		9	
	H ₂ /CO molar ratio		1.70	
			Methanol	89.2
Selectivity to product (% molar)		DME	0.1	
		Methane	0.1	
		H ₂ O	10.6	
DME synthesis	Temperature (K)		593	
	Pressure (MPa)		2.0	
	Methanol conversion (%)		85	
	Selectivity to DME		1	
DME hydrocarbonylation	Temperature (K)		493	
	Pressure (MPa)		1.5	
	H ₂ /CO molar ratio		1.57	
	DME conversion (%)		48	
			Methanol	45.0
	Selectivity to product (% molar)		Ethanol	38.0
		Methyl acetate	6.5	
		CO ₂	10.5	

Table 4. Process conditions for the dehydration reactor (adapted from [43]).

Temperature (K)		613	
Pressure (MPa)		0.48	
Ethanol conversion		1	
Carbon selectivity (%)		CH ₄	0.10
		C ₂ H ₄	96.50
		C ₂ H ₆	0.50
		C ₃ H ₆	0.05
		Butenes	2.40
		Acetaldehyde	0.20
		Coke	0.25

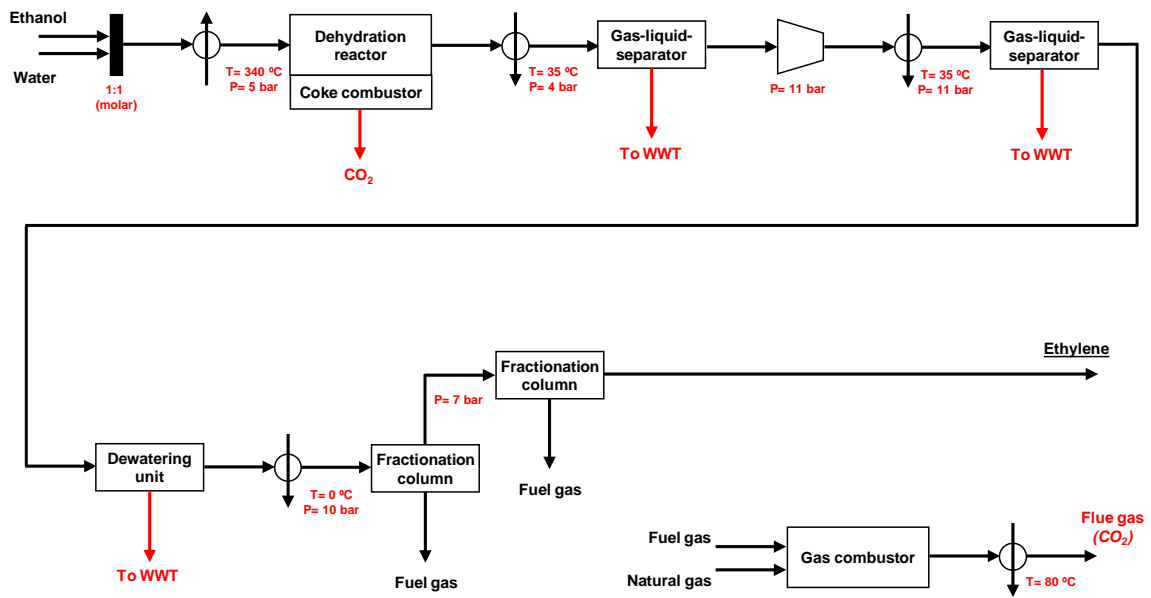


Figure 5. Process flowchart for the ethanol dehydration section.

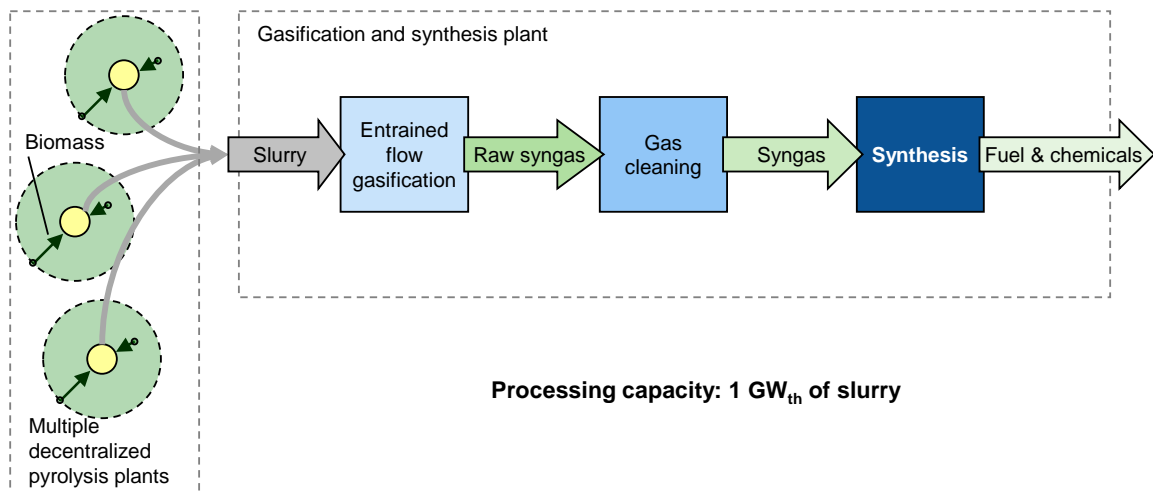


Figure 6. Overview of the bioliq® concept.

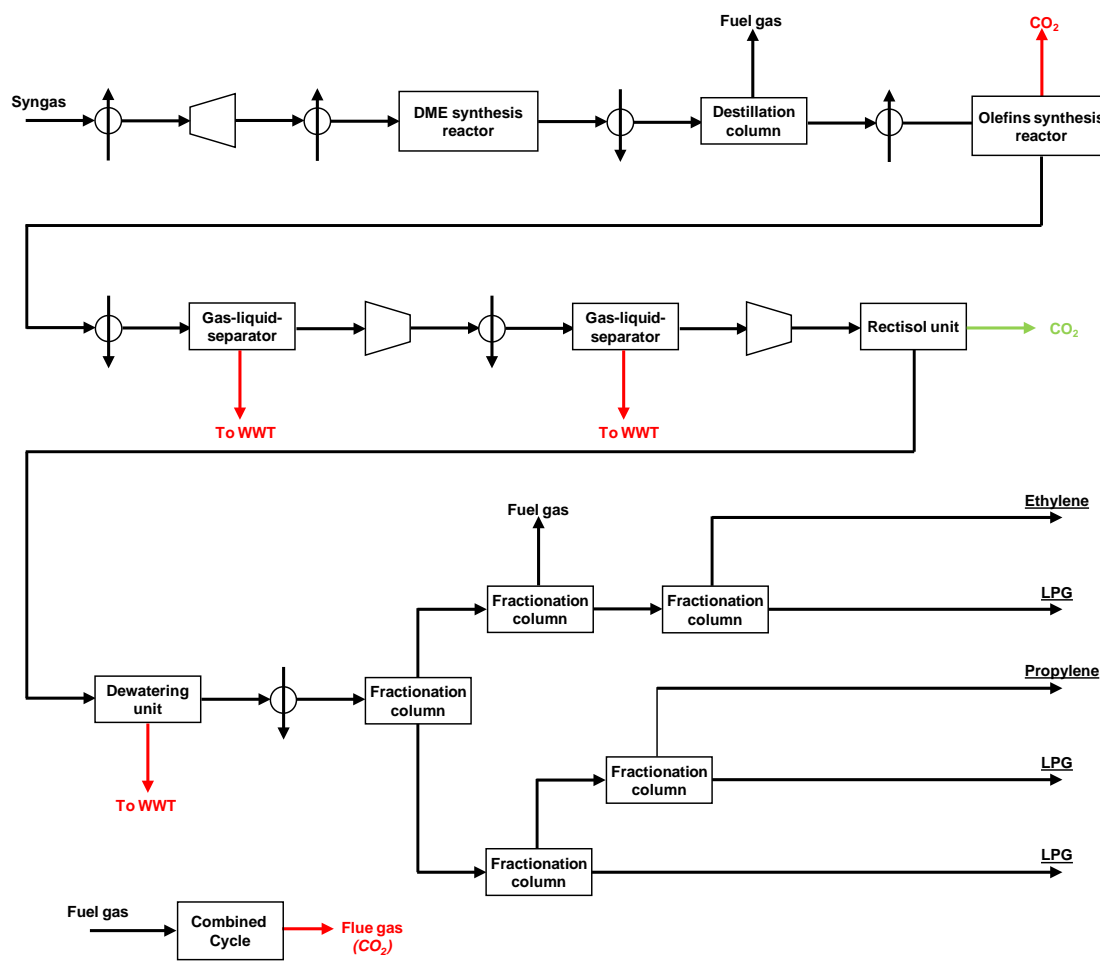


Figure 7. Process flowchart for the DME-to-olefins alternative (adapted from [8]).

Table 5. Process conditions for the ethylene production from syngas [8].

DME synthesis	Temperature (K)	523	
	Pressure (MPa)	3.5	
	CO conversion (%)	85	
	H ₂ /CO molar ratio	1.0	
	Product distribution (% mass)	DME	49.3
Methanol		1.4	
CO ₂		48.8	
H ₂ O		0.5	
DME-to-olefins	Temperature (K)	996	
	Pressure (MPa)	0.4	
	DME conversion	1	
	Inert compounds (% v/v)	39.1	
	Hydrocarbon product distribution (% mass)	Ethylene	45.1
		Propylene	38.7
Other light gases		7.9	
Butenes		8.3	

3. Methodology

In order to conduct the technoeconomic assessment for the case studies, the mass and energy flows within the system boundaries are analyzed first. For this purpose, the process simulation software Aspen Plus is used. The mass and energy flow balancing builds up the foundation for the economic assessment. Fixed capital investment (FCI) estimated for the considered case studies are derived using the determined capacities. Investment dependent costs together with personnel and other operating costs, as well as revenues from by-products, lead to specific production costs for the considered products in each case

3.1. Process modeling

Below, the most important criteria and assumptions used to simulate the considered case studies are outlined. The thermodynamic methods used to model the direct and indirect production of ethanol (case studies 3 and 4) are described in [7, 6]. The dehydration of ethanol is modeled using the equation of state of Redlich—Kwong—Soave with Boston—Mathias modifications (RKS—BM) [49]. The thermodynamic methods used to model the DME-to-olefins conversion are described in [8]. The CO₂ capture, when applicable, was previously modeled in their corresponding studies ([6] for case study 3, [7] for case study 4 and [8] for case study 5).

The specific product yields of the ethanol dehydration reactor (RYield) are calculated in a spreadsheet using technical data from [43] and result in the distribution of products presented in Table 1. An analogous procedure was used to specify product yields in the DME-to-olefins reactor [8]. In case study 3, product distribution was calculated using a proprietary MoS₂ catalyst patented by Abengoa Bioenergy [6]. In case study 4, product distribution was calculated using experimental data [7].

For all case studies, rigorous fractionation columns (RadFrac) are used to give accurate results in the recovery of products and specifically for the ethylene recovery (modeled in this study). Column design and modeling in terms of molar split fractions, optimization of utility consumption and the thermal integration of columns were performed according to Smith [50] and thermal integration of the plant is described in [6, 7].

3.2. Fixed capital investment estimate

The economic assessment aims to determine ethylene production costs for the five case studies. To achieve this goal, the FCI for the ethanol dehydration, applicable in case studies 1-4, is estimated in this study (case study 5 was previously analyzed [8]). All equipment components are designed according to the mass and energy flows. As previously mentioned, in case studies 1 and 2 the FCI is calculated for a range of plant capacities, whereas in case studies 3 and 4 the FCI is calculated for a determined plant capacity. The FCI for case study 5 (DME-to-olefins) was also estimated for a specific plant capacity [8].

The investment data for the main equipment components are summarized in Table 6. The investment data for equipment components not listed in Table 6, e.g. heat exchanger and distillation columns, are calculated according to [51, 53]. The investment data are converted into €, using the yearly average exchange rate of the respective year [54], and updated to the year 2011. To account for price developments of equipment components, the price index from Kölbel/Schulze [55] is used. The presented results in section 4 for capital investment and production costs can be converted to US\$ by using the average 2011 exchange rate of 1.401 US\$/€.

Based on the investment data for the main equipment, the total capital investment of the ethanol dehydration plant can be estimated using ratio factors for direct and indirect capital investment according to [51], as explained in previous publications of the authors [48, 56]. Table 7 shows the assumed ratio factors for the control system, piping and further direct capital investments as well as the ratio factor for indirect capital investments, such as engineering or legal expenses. The ratio factors are selected according to process conditions, design complexity and required materials in this study. The applied ratio factor method implies uncertainties of $\pm 30\%$ [51].

3.3. Production cost estimate

The annual production costs consist of investment dependent, personnel and operating costs, as well as revenues from by-products (only in the DME-to-olefins case). The investment dependent costs in turn are comprised of capital costs, maintenance and tax, as well as insurance and interests on working capital. Ethanol, biomass, catalysts, cooling water and electricity make up the consumption dependent costs of each case study. The composition of the annual production costs is calculated as in [48, 56], where further information can be found. In case studies 1 and 2, the annual production cost is also evaluated for their corresponding range of plant capacities.

The personnel requirement and costs estimation are based on previous studies [44, 56, 57] based on the German workforce. Further economic assumptions used for the economic assessment of ethanol dehydration are presented in Table 8.

The production costs of ethanol in the case studies, including ethanol dehydration, have been selected subject to the origin of the ethanol. Table 9 shows the price of ethanol feedstock for each case. These production costs do not include transportation of ethanol to the dehydration plant gate.

The production cost of 2nd generation ethanol via the direct route has been evaluated in [6] and the 2nd generation ethanol via the indirect route in [7]. Both are based on biomass feedstock costs of 66 US\$ per dry ton. The production cost of ethylene in the DME-to-olefin case study

has been evaluated in a previous publication [8] and is based on biomass feedstock costs of 71 € per dry ton.

Table 6. Summary of investment data for main equipment components (ethanol dehydration plant).

Description	Base scale	Unit	M€ ₂₀₁₁	Scaling factor	Reference
Dehydration reactor	2386	kmol of ethanol feed/h	2.8	0.65	[32]
Cryogenic system	13.0	MW _{th}	10.3	0.70	[51]
Compressor	1.40	MW _e	0.6	0.67	[52]
Steam generator	38	MW _{th}	6.5	0.60	[51]

Table 7. Ratio factors for direct and indirect capital investments (adapted from [51]).

<i>Direct investments</i>	%
Investment for installed equipment	100
Instrumentation and control	24
Piping	46
Electrical systems	8
Buildings	12
Yard improvements	7
Service facilities	48
Total direct investment	245
<i>Indirect investments</i>	%
Engineering and supervision	22
Construction expenses	28
Legal expenses	3
Contractor's fee	15
Contingency	30
Total indirect investment	98
Fixed Capital Investment (FCI)	343

Table 8. Summary of economic assumptions.

Parameters for investment dependent costs		
Capacity factor	%	80
Expected lifetime	Years	20
Depreciation (no scrap value)	Linear	–
Interest rate	%	7.0
Working capital	% of FCI	5.0
Maintenance costs (average)	% of FCI	3.0 – 3.6
Insurance & taxes	% of FCI	2.0
Prices for consumables		
Electricity [58]	€/MWh	85.95
Natural gas [58]	€/MWh	44.50
Cooling water [32]	€/m ³	0.26
Waste water treatment [48]	€/m ³	0.32
Dehydration catalyst [32, 59]	€/kg	113

Table 9. Summary of feedstock ethanol price for case studies 1-4.

		Price	Source
Case study 1	Commercial price of bioethanol ^a (1 st generation ethanol)	0.72 – 0.74 €/L	Europe [9]
		2.41 – 2.68 US\$/gallon	USA [9]
		0.51 – 0.62 US\$/L	Brazil [9]
		2 nd generation biochemical ethanol (via enzymatic hydrolysis)	0.95 US\$/L
Case study 2	2 nd generation ethanol biochemical ethanol (via syngas fermentation)	0.6 €/L	Fornell et al. [11]
		1 US\$/gal	Coskata [25]
Case study 3	2 nd generation ethanol via thermochemical processing (direct route)	0.710 US\$/L	Villanueva et al. [6]
Case study 4	2 nd generation ethanol via thermochemical processing (indirect route)	0.555 US\$/L	Haro et al. [7]

^a Data referred to September 2012.

4. Results

The following section compares the resulting mass and energy balances as well as fixed capital investment and production costs estimates for the considered case studies.

4.1. Mass and energy balances

Table 10 shows the results for the mass and energy balances for all case studies. In case studies 1 and 2, the ethanol input to the dehydration plant ranges from 150 to 500 ML/year and from 300 to 1000 ML/year respectively (see 2.1.1. and 2.1.2.). For case studies 3 and 4, the ethanol input is the value from the corresponding assessments [7, 6] and the original biomass input is also included in the system boundaries. In case study 5, all data refer to the previous publication by the authors [8], which has a fixed biomass input.

The energy efficiency to ethylene (and total products) in Table 10 is calculated according to Eq. (2), where the net input of electricity and natural gas are added when necessary. The electricity input is converted to an HHV equivalent assuming a conversion efficiency of 39%.

For case studies 1-4, in those with a dehydration plant, an additional input of both natural gas and electricity is needed. In case study 5, only electricity is imported to the plant. The energy efficiency of ethanol dehydration is quite high, so the low values of case studies 3 and 5 are due to the previous processing. Case study 4 achieves the best energy efficiency. However, the corresponding ethylene production is close to that in case study 5, in which the efficiency to ethylene halves, as a result of the different biomass input in each case study. In case study 5, the co-production of propylene and LPG enhanced the global efficiency of process as in case study 4. Case study 3 achieves the lowest efficiency despite the co-production of higher alcohols.

$$\text{Energy efficiency (HHV)} = \frac{\text{product(s) (MW}_{th})}{\text{biomass (MW}_{th}) + \frac{\text{electricity consumed (MW}_e)}{0.39} + \text{natural gas (MW}_{th})} \quad (2)$$

Table 10. Mass and energy balances for the considered case studies.

	Case study				
	1	2	3	4	5
Input to system boundaries					
Biomass in t/day (MW HHV)	N/A	N/A	2140 (500)	2140 (500)	3456 (1000) ^a
Ethanol in t/h (MW HHV)	16.9 – 53.2 (148 – 495)	33.8 – 112.6 (297 – 990)	14.5 (112)	25.9 (199)	N/A
Ethanol in ML/year	150 – 500	300 – 1000	129 ^b	230 ^b	N/A
Electricity in MW	4 – 13 ^c	8 – 26 ^c	3	6	27.0
Natural gas in MW	7 – 24 ^c	15 – 49 ^c	6	11	0
Output from system boundaries					
Ethylene in t/h (MW HHV)	9.9 – 38.9 (137 – 456)	20.5 – 68.2 (273 – 911)	8.5 (117)	15.1 (210)	16.6 (230)
Propylene in t/h (MW HHV)	N/A	N/A	N/A	N/A	14.3 (199)
LPG in t/h (MW HHV)	N/A	N/A	N/A	N/A	6.0 (84)
Energy efficiency					
From biomass to ethylene (total products) in % HHV	N/A	N/A	22.7 (30.7)	40.0	16.5 (41.1)
From ethanol to ethylene in % HHV		81.8			N/A

N/A: not applicable.

^a Referred to bio-slurry.

^b These values differ from references [7, 6] due to the change in the capacity factor (see Table 8).

^c Ethanol production is not included.

4.2. Fixed capital investment

The results of the fixed capital investment (FCI) estimation corresponding to the system boundaries of this study are illustrated in Figure 8 and Figure 9. The FCI of case studies 1 and 2 is presented for both extremes of considered plant capacity (see Table 10). The FCI for case studies 3-5 is notably larger than the FCI for case studies 1 and 2, which is a consequence of the different system boundaries used in the assessment (see Figure). In order to compare the FCI, the dehydration plant of case studies 3 and 4 is also shown separately in Figure. The FCI of case study 5 is 31% and 72% larger compared to case studies 4 and 3, respectively. This difference is mainly due to the different capacities of biomass processing in these cases.

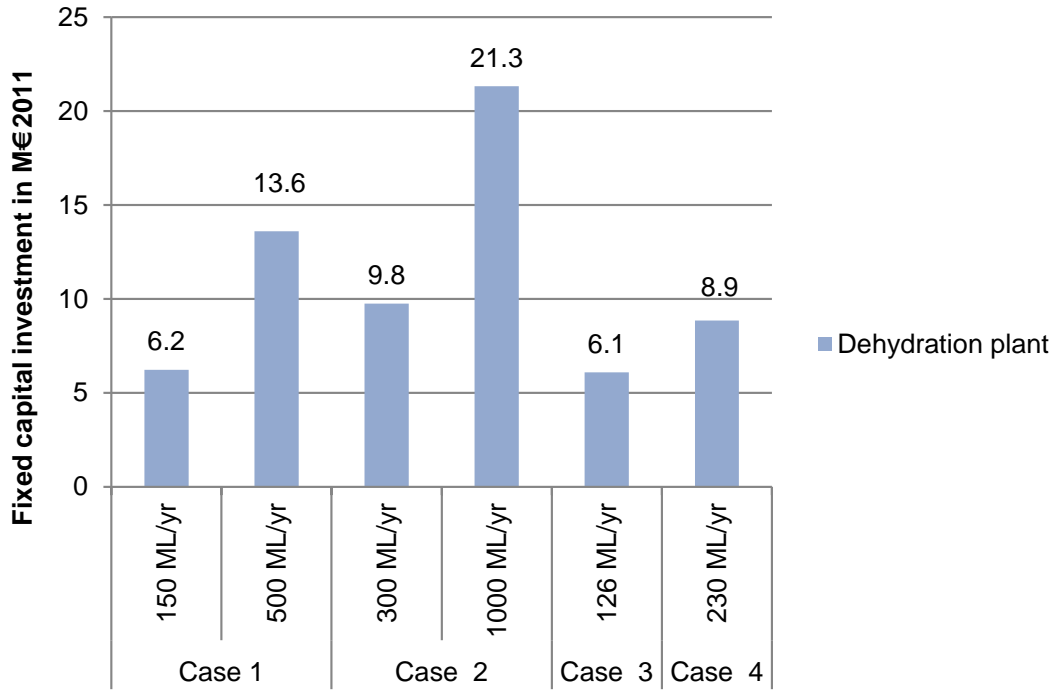


Figure 8. Fixed capital investment for the dehydration plant in case studies 1-4.

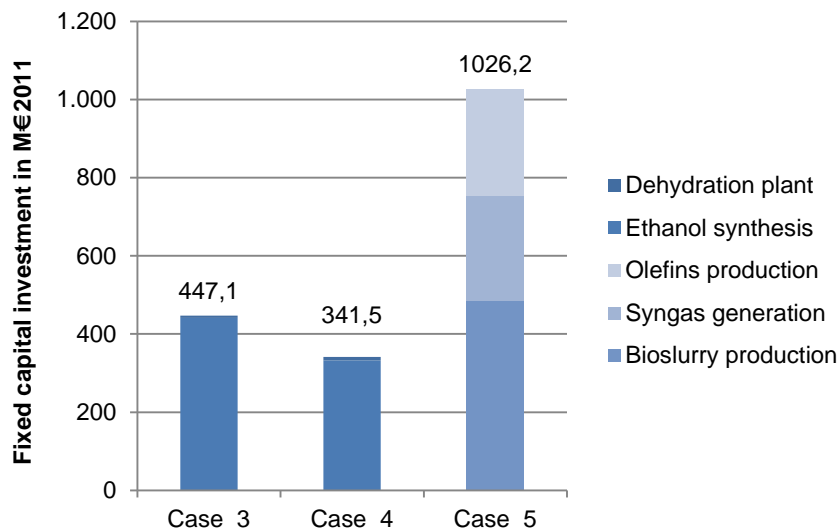


Figure 9. Fixed capital investment for case studies 3-5.

4.3. Production cost estimate

Figure 10 shows the specific production cost of ethylene for all alternatives in case study 1, i.e. using commercial prices from the EU, USA and Brazil, and for both extremes of plant capacities. Obviously, the lower the considered price of ethanol, the lower the production cost of ethylene. The contribution of ethanol cost to the total production cost of ethylene is about 91% for the lowest capacity using European ethanol and about 85% for the highest capacity using Brazilian ethanol.

Figure 11 shows the specific production cost of ethylene for all alternatives in case study 2, i.e. using estimated ethanol prices based on 2nd generation processes and for both extremes of plant capacities. As in case study 1, the price of ethanol feedstock is critical for the production costs of ethylene. For 2nd generation processes based on enzymatic hydrolysis, the production costs of ethylene ranges are about the same or slightly larger than in case study 1. However, if the considered price for ethanol via syngas fermentation were accurate, then this process could produce ethylene at a half cost compared to using commercial Brazilian ethanol.

Figure 12 shows the specific production cost of ethylene for all alternatives in case studies 3-5. The lowest value corresponds to case study 4 and the highest to case study 3. The differences between both cases are a result of the lower price of ethanol in case study 4 and the higher capacity of the dehydration plant. In case study 5, syngas, instead of ethanol, is the main contribution to the production costs of ethylene and represents 85% of the total production cost (revenues excluded).

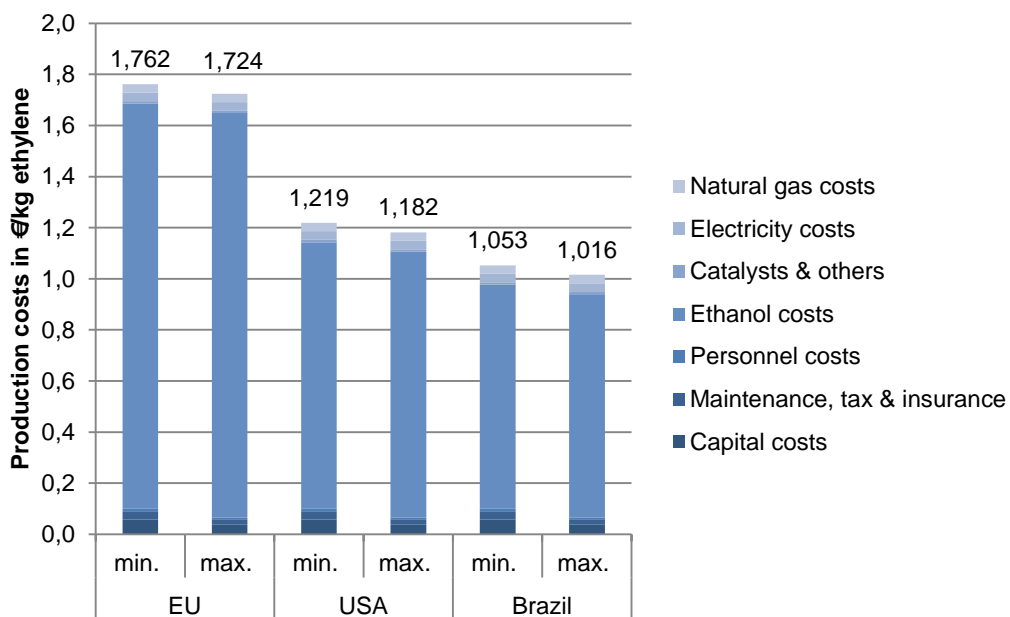


Figure 10. Specific production costs for case study 1.

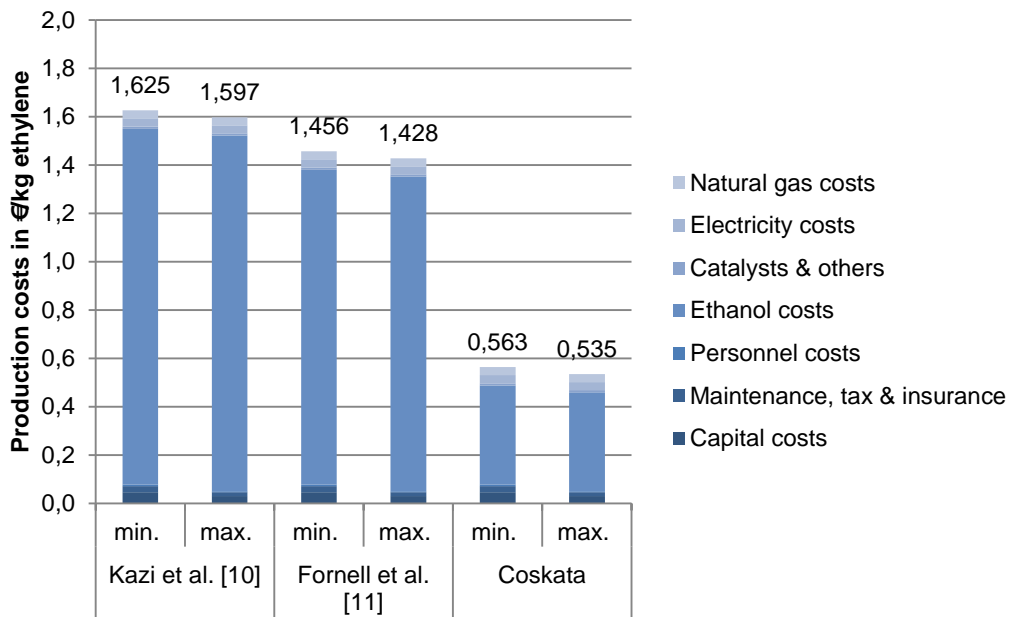


Figure 11. Specific production costs for case study 2.

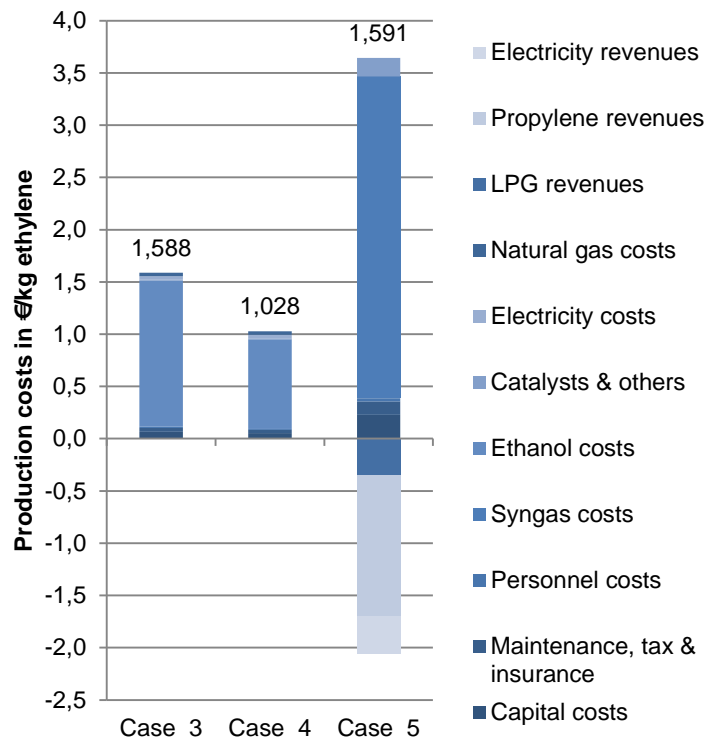


Figure 12. Specific production costs for case studies 3-5.

5. Discussion

The production of ethylene from ethanol is highly dependent on the price of ethanol feedstock (minimum 85% of production cost), which should be below 0.45 €/L in order to achieve profitability regardless of the origin of the ethanol (case studies 1-4). This ethanol price is significantly below the current price of European ethanol, similar to USA ethanol and higher than Brazilian ethanol. Nevertheless, the origin of the ethanol plays a crucial role in the future development of processes using ethanol as a platform chemical. The availability of biomass, which is actually the bottleneck for all biomass-derived products, along with the future regulation of biofuels, are the keys to the development of future bio-ethylene production. Despite the higher production cost of ethylene in case study 2 (2nd generation ethanol via enzymatic hydrolysis), the future regulations on biofuels could plunge the profit of current 1st generation ethanol by withdrawing current subsidies or limiting biomass availability. Moreover, the volatility of the ethylene price brings more uncertainty regarding the profitability of an ethanol-to-ethylene plant. For the DME-to-olefins case, the production of ethylene is not related to that of ethanol, the process is well integrated and includes the co-production of propylene and LPG. However, the uncertain availability of cheap lignocellulosic biomass and the volatility of the ethylene market price are still applicable in this case.

The production of ethylene from biomass is profitable if Brazilian ethanol is used. In the case of using ethanol via thermochemical processing (only for indirect synthesis, case study 4), the resulting ethylene production costs are also below the minimum ethylene market price in 2011 and 2012 (about 1100 €/t). However, if only the currently feasible processes for the production of ethylene from biomass are considered, the use of Brazilian ethanol would be most likely, as demonstrated by Braskem in their *green*-polyethylene plant [14]. The use of bio-ethanol for the production of chemicals reveals a controversy about the possible uses of bioethanol. Should the current use of bioethanol as a renewable fuel be diverted into the production of chemicals or should other new uses of bioethanol (as a platform chemical) be satisfied exclusively with the increase in bioethanol production? Implications of this controversy are quite serious, since the alternative uses of ethanol as a platform chemical might take over the up-to-date paradigm of bioethanol as one of the most important biofuels for the future.

5.1. Integration of ethylene production with ethanol production plants

As mentioned in section 2.1.1., the integration of ethylene production with an existent ethanol production plant has been disregarded in this study. The main reason is the economies of scale (current ethanol plants have a plant capacity of around 50 ML/year [9]). However, the integration of a dehydration plant in an ethanol production facility could benefit from important advantages if both plants are simultaneously designed and operated as a whole. Like in a dehydration plant, the ethanol stream must be diluted with water (see section 2.1.5.). If the whole production of ethanol was fed to the dehydration plant, no azeotropic distillation would be needed; which would lead to an important reduction in both investment and operating costs. The product

stream from biomass fermentation would only require a soft distillation in order to enhance the concentration of ethanol up to the dehydrator requirements (see Table 4). The benefits of this integration were first commented on in the BETE (BioEthanol-To-Ethylene) process in the 1980s [12].

5.2. Integration of BECCS and comparison of the case studies

For the inventory of CO₂ emissions, only those within the system boundaries of this study are taken into account; except for case studies 1 and 2, where estimations for the synthesis of ethanol are also given. It is considered that only the CO₂ that is already captured in these cases or available at high purity will be suitable for transport and storage (marked green in Figure 3, Figure 4 and Figure 7). Hence, other sources of CO₂, like combustion gases are disregarded since they represent neither an advantage from CCS in power plants nor a benefit to the process economics. The extra energy input for CO₂ compression is assumed to come from the grid. The calculations of the CO₂ sequestration costs (comprising compression, transportation and storage) are according to the methodology described in section 3.

Table 11 shows the summary of total CO₂ emissions and integration of BECCS in the case studies. The results of the integration of BECCS are in agreement with a recent study by Meerman et al. [60], which assesses the sequestration of CO₂ in facilities using a steam methane reformer (as in case study 4), and in general with the data published by the IEA in 2011 [3], where the reduction of the capital cost for CO₂ capture (pre-combustion) is balanced with the inclusion of transportation and storage costs. The available CO₂ for storage fluctuates from about 70% of total CO₂ emissions in case study 3, where most CO₂ is captured by the Selexol unit (see Figure 3); to about 24% in case study 4, where the Amines unit is used only to remove the excess CO₂ in the ethanol synthesis loop (see Figure 4). In case study 5, there are two sources of CO₂ available for storage, both using Rectisol technology (see Figure 5). Although each case study uses a different capture technology, the CO₂ sequestration cost, i.e. the costs of capture (only compression), transportation and geological storage, are slightly different. In case study 2, considering the biochemical production of ethanol (where total emissions of CO₂ are externally given), it is possible to calculate the available CO₂ for storage (19% of total CO₂ emissions), which is much lower than in the case of thermochemical processing (case studies 3-5).

Table 11. Summary of CO₂ emissions and integration of BECCS in the case studies.

		Case study				
		1 ^a	2 ^a	3	4	5
		(500 ML/yr)	(1000 ML/yr)			
CO ₂ emissions in t/h	Pyrolysis	N/A	N/A	21.9	N/A	89.9
	Gasification & conditioning	N/A	N/A	101.4	61.8	101.5
	DME-to-olefins	N/A	N/A	N/A	N/A	104.3
	Ethanol synthesis	<i>54.6 (only fermenter [61])</i>	<i>500.7 (total [62])</i>	12.1	51.2	N/A
	Ethanol dehydration (neutral CO ₂)	3.7	17.5	1.0	1.7	N/A
	Ethanol dehydration (total emissions)	9.6	45.4	2.5	4.4	N/A
	Derived from the input of electricity ^b	6.5 ^c	13 ^c	1.5	3	13.5
	Total neutral CO₂ emissions	58.3	126.8-518.2	136.4	114.7	295.7
Total CO₂ emissions	-	559.1	139.4	120.4	309.2	
CO ₂ available for sequestration in t/h	Gasification & conditioning	N/A	N/A	101.4	0	88.0
	Synthesis	<i>54.6</i>	<i>109.3</i>	0	31.3	37.4
	Total	54.6	109.3	101.4	31.3	125.3
Technology for CO ₂ capture	N/A	N/A	Selexol	Amines	Rectisol	
Extra input of electricity due to the capture in MW	5.9	11.8	10.9	3.4	13.5	
Extra CO ₂ emissions due to the capture in t/h ^b	3.0	5.9	5.5	1.7	6.8	
Total CO₂ sequestration costs in €/t^d		26^f		33	30	39

^a In these cases the ethanol production, as well as the potential capture of CO₂ is not included in the system boundaries of this study. The given values outside system boundaries are estimated from the literature and shown in italics.

^b Assumed to be 0.5 t of CO₂ per MWh of electricity (a typical CO₂ emission per electric MW in Europe).

^c The production of ethanol is not included.

^d It includes CO₂ transportation (4 €/t) and storage (14 €/t) taken from the IEA [63].

^f A rough estimation based on [64].

5.3. Comparison of all case studies in terms of BECCS integration and plant capacity

For case studies 1 and 2, the sensitivity is represented as a function of the plant capacity, whereas for case studies 3-5 it is represented as a function of the selling price of CO₂ credits. It must be noted that the possibility of extra revenues due to CO₂ sequestration is not taken into account for case studies 1 and 2. Although the capture and storage of CO₂ in these processes seems favorable, the small capacity and the geographical dispersion of ethanol plants are the main obstacles for its implementation [61, 64]. In comparison to cases considering thermochemical processing, Lindfeldt and Westermark [65] concluded that CO₂ capture is more realizable. Currently, the main uses of CO₂ from ethanol plants are not sequestration but food processing and preservation (e.g. carbonated beverages and refrigeration), representing more than 30% of the merchant CO₂ market in USA [64].

Figure 13 shows a global outlook on the sensitivity analysis for all case studies considering BECCS. In order to compare all the case studies with each other and with the commercial price of ethylene, a transition zone (gray) has been added representing the variation of the ethylene market price from 2011 to the present along with the price of ethanol feedstock for all alternatives in case studies 1-4. For 1st generation ethanol (case study 1) the production of ethylene is profitable at current market prices, if Brazilian ethanol is used as feedstock. European ethanol should be disregarded, as it would produce ethylene at costs higher than the current commercial price. In the case of ethanol from USA, the resulting ethylene production cost would lie in the range of the ethylene market price between 2011 and 2012. The future price of 2nd generation ethanol (case study 2) is still uncertain so the curves are illustrated using dashed lines for the alternatives via enzymatic hydrolysis and a dotted line for the more uncertain case of syngas fermentation (Coskata). In comparison to case study 1, the curves decrease downwards more steadily, as a result of the higher considered capacities. Only in the case of ethanol from syngas fermentation, might the resulting ethylene be cost-competitive and it would halve the current ethylene market price. For ethanol using the thermochemical processing of biomass and direct synthesis from syngas (case study 3), the resulting ethylene price is significantly above the market price. However, assuming the possibility of selling CO₂ credits, the process would produce cost-competitive ethylene with CO₂ credits above 75 € per tonne of sequestered CO₂. In the similar case of ethanol from thermochemical processing but using indirect synthesis (case study 4), the process is profitable even without the sale of CO₂ credits. For case study 5, using thermochemical processing of biomass and syngas conversion via DME-to-olefins, the results are close to those of case study 3, except for the required CO₂ credits price. In this case, a CO₂ credit price above 150 €/t would be needed to achieve a cost-competitive production of ethylene.

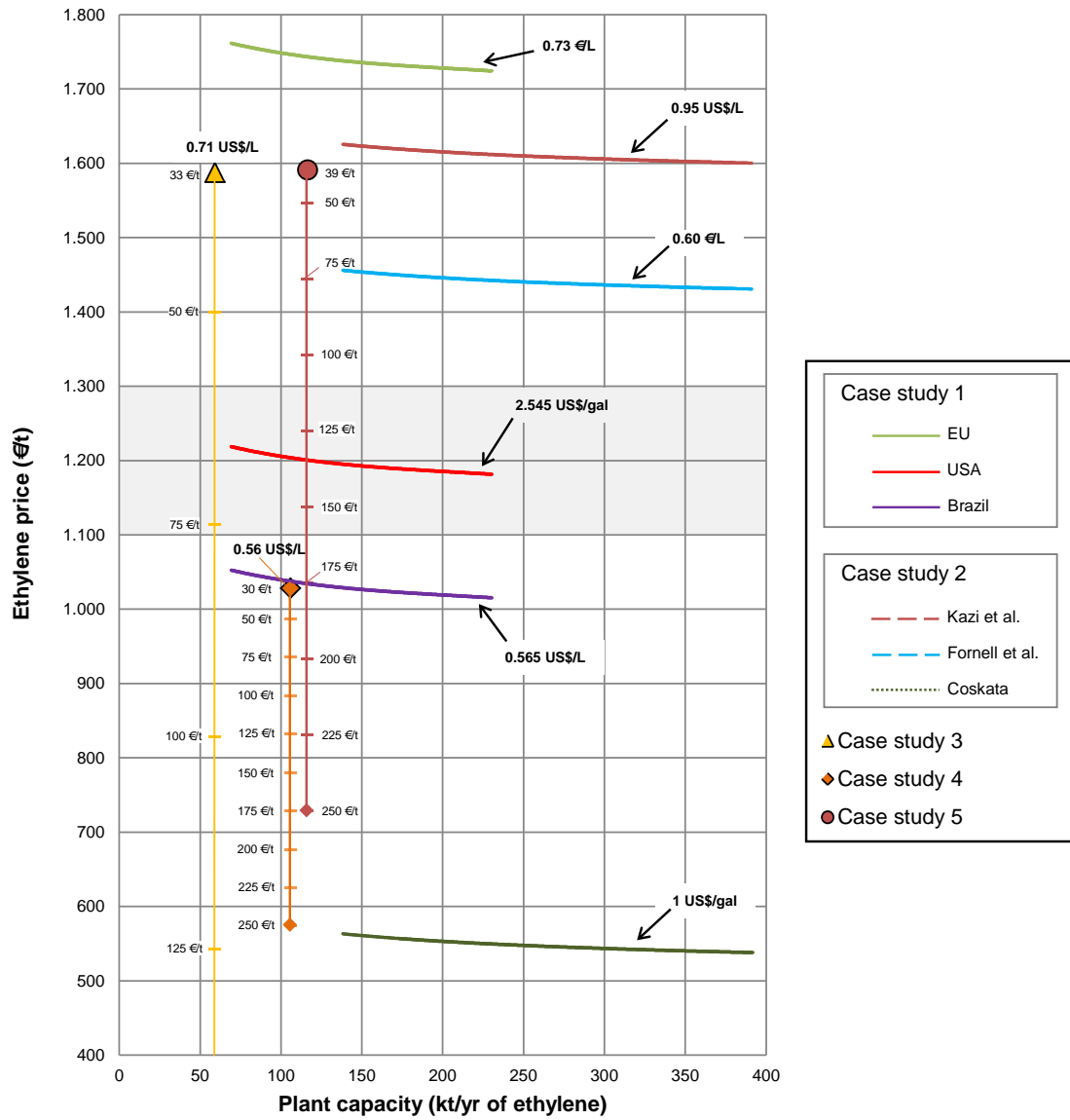


Figure 13. Sensitivity of ethylene price for the case studies as a function of plant capacity and market price of future CO₂ credits (based on sequestered CO₂).

6. Conclusions

The presented work assesses the technical and economic viability of potential processes to produce ethylene from biomass using currently or potentially applicable technologies using technical and economic data from the bioliq[®] project. Two main routes are identified to this end using ethanol or DME as platform chemicals. For all case studies using ethanol, it can be concluded that the price of ethanol feedstock is crucial. Only Brazilian ethanol and the estimated price of ethanol via the indirect synthesis of syngas would enable the cost-competitive production of ethylene. However, the development of new uses for ethanol different to the biofuel application, reveals a controversy if current bioethanol should be diverted into the production of chemicals or these new uses should be satisfied only with a future increase in bioethanol production. For the case study using DME, the resulting price of ethylene is above the commercial ethylene price, but it does not require ethanol. If BECCS (Bioenergy with Carbon Capture and Storage) is taken into account for the case studies, the results would be substantially enhanced.

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