

Bio-ethylene from sugarcane as a competitiveness strategy for the Brazilian chemical industry

Camilla C.N. Oliveira[®], Pedro R.R. Rochedo[®], Energy Planning Program, Graduate School of Engineering, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Rio de Janeiro, Brazil **Rajat Bhardwaj[®]**, Sustainable Process and Energy Systems Department, TNO, Delft, The Netherlands **Ernst Worrell[®]**, Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, The Netherlands

Alexandre Szklo[®], Energy Planning Program, Graduate School of Engineering, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Rio de Janeiro, Brazil

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Abstract: The urgency with which the world economy needs to be decarbonized could lead to the emergence of regions with the capacity to produce renewable feedstock such as biomass. The competitiveness of these regions could result from their ability to produce high value-added chemicals at the lowest cost. The biomass embodied in a chemical product could reduce carbon emissions, leading to net CO_2 removal. The aim of this study was to test the hypothesis that bio-ethylene could make the Brazilian chemical industry more competitive. This would be achieved by applying the revenues from carbon credits associated with using ethanol and sugarcane bagasse as feedstocks for bio-ethylene production. Three production routes were compared according to their estimated cost of production in Brazil under a simplified life-cycle analysis: sugar-cane-derived ethanol to ethylene (with and without CO_2 capture and storage – BECCS); bio-methanol to olefin; and conventional steam cracking of naphtha. When associated with the production of long-lasting materials, the ethanol-to-ethylene with BECCS route achieved the lower CO_2 break-even price (US\$75/t CO_2), followed by ethanol to ethylene without BECCS (US\$82/t CO_2) and bio-methanol to ethylene (US\$106/t CO_2). Our findings highlight the advantage for the Brazilian chemical industry of implementing a national or, even better, a global carbon-pricing instrument. © 2019 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: bio-ethylene; sugarcane; BECCS; life cycle analysis

Introduction

he Paris Agreement signed at COP21 in December 2015 sets a global objective of limiting the rise in the average global air temperature at the Earth's surface to 'well below 2 °C' above pre-industrial levels.¹ According to the IPCC Synthesis Report,² no more than about 1000 Gt CO_2eq should be emitted between 2011 and 2100 to keep the rise in temperature below 2 °C with a probability of 66% or more. Since 2011, about 200 Gt CO_2eq has been emitted, leaving

Correspondence to: Camilla C. N. Oliveira, Energy Planning Program, Graduate School of Engineering, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco C, Sala 211, Cidade Universitária, Ilha do Fundão, 21941-972 Rio de Janeiro, RJ, Brazil. E-mail: camillacnoliveira@gmail.com



about 800 Gt CO₂eq, which is the total amount that can be emitted in the future if global temperatures are to be kept within the desired limit of 2 °C. Current emissions (including land-use change emissions) are already close to 40 GtCO₂ eq per year.³ Moreover, if the target of limiting the temperature increase is set at 1.5 °C, instead of 2 °C, the challenge becomes even more difficult,⁴ highlighting the urgency of considering various technological options to achieve appropriate net carbon-dioxide removal (CDR).^{5,6}

The chemical and petrochemical sector is the largest industrial energy user, accounting for 28% of the world's industrial final energy consumption,⁷ 10% of the world's total final energy consumption,⁷ and 7% the of greenhouse gas (GHG) emissions associated with industry.8 At the same time, the climate debate in this sector is one of the key 'blind spots' in the global energy debate,⁹ and differs from what happens in other industrial sectors. This sector uses fossil fuels both for energy as well as a feedstock for the production of materials,¹⁰ resulting in a possible industrial process to capture carbon. As the chemical products are used in a wide variety of applications, the reduced emissions in this sector contribute to reducing the emissions in many other sectors through their products, adding value to their value chain.^{10,11} For instance, plastic insulation materials such as polystyrene or polyurethane result in energy savings from home heating and cooling and related CO₂ savings.¹¹

Chemical production based on low-cost, readily available feedstock has been a cornerstone of value creation in the industry, as seen in the USA, with its cheap shale gas, and in the Middle East, with stranded gas reserves. They represent the low-cost champions for key petrochemicals.^{9,12,13} Companies around the world are therefore locating themselves in those regions to take advantage of cheap feedstock.^{12,14} However, the urgency with which the world economy needs to be decarbonized could lead to the emergence of other regions with renewable feedstock such as biomass.^{15,16} This could become a source of competitiveness that would produce high value-added chemicals at low cost, including the cost of GHG emission abatement.

Bio-based chemicals could significantly reduce the environmental impact of the chemical industry, lower many countries' dependence on fossil fuels, and stimulate local economies.¹⁷ Moreover, the conversion of biomass into a chemical product can be a CDR option.^{18–20} This is particularly important as CDR has become widely selected by integrated assessment models (IAMs) to meet the requirements of keeping the global temperature rise under the 2 °C limit.^{1,21–24}

Brazil is one of the world's major agricultural producers²⁵ and supports a vast production of plantation crops like sugarcane, the predominant feedstock for its ethanol industry.²⁶ Along with the USA, Brazil leads the world in production of ethanol with those two countries accounting for 85% of global ethanol production.²⁷ Historically, Brazil has had the lowest production cost (\$0.16–0.22/l)²⁸ compared with the USA (\$0.25–0.40/l),²⁸ Europe (\$0.36–0.57/l),²⁸ or China (\$0.32/l).²⁸ However, with the recent rapid increase in ethanol production in the USA (ethanol production there increased 9,100% from 1980 to 2018, surpassing Brazilian production in 2006²⁷) combined with the decreased investment in ethanol production in Brazil (since 2009),²⁹ both countries currently report similar ethanol production costs (between \$0.51–0.58/Lge (liter of gasoline equivalent) in the USA and \$0.54–0.62/Lge in Brazil).³⁰

Despite its current similar production costs compared to sugarcane ethanol,³⁰ corn ethanol does not generate enough lignocellulosic material for chemical production. This also means that the Brazilian sugarcane industry can use both ethanol and surplus bagasse to produce chemicals. Brazil rates as a top producer of soybeans and coffee.³¹ The country generates significant amounts of biomass residues from harvesting and processing agricultural products such as sugarcane, soybeans, and rice.³²

Interestingly, the use of biomass is well regarded for energy production such as bioenergy in transport, for heating or cooking in households, or for conversion into electricity.^{26, 33–35} Some IAMs have identified the importance of biomass in the energy system to meet emission reduction targets.^{36–39} The scientific literature has traditionally dealt with biomass conversion to energy from the perspective of the energy-food dilemma.^{40–42} However, the scientific literature still lacks studies that evaluate CDR technologies that convert biomass into chemical products.

Given the abundant source of biomass in Brazil along with the advantage that the chemical sector has in capturing CO₂ in its final products, this study aims to evaluate the potential gain in competitiveness of the Brazilian chemical industry by processing biomass. At present, the main sources of competitive advantage in the petrochemical sector are cost and, to a lesser extent, economies of scale.⁴³ The hypothesis proposed in this study is that, if the carbon price is high enough, the Brazilian petrochemical industry can become competitive in cost through a quality premium price due to environmental differentiation (fewer GHG emissions when compared with fossil-fuel-based production).

To test this hypothesis, ethylene was selected as the case study. Ethylene is by far the most important building block in the petrochemical industry with a wide applicability.⁴⁴ The global production capacity of ethylene exceeds 140 million tonnes per year.⁴⁵ Ethylene represents 51% of total olefin production in Brazil.⁴⁶ Most of the ethylene is polymerized into polyethylene plastics such as HDPE (high-density polyethylene), LLDPE (linear low-density polyethylene), and LDPE (low-density polyethylene) but it is also used for the production of cosmetics, solvents, and paints. Three ethylene production routes were compared according to their estimated levelized cost of production in Brazil and their environmental impact was examined using a simplified life cycle analysis, to investigate whether the use of biomass as feedstock could become a source of revenue in scenarios with different CO₂ prices. (The levelized cost of each bio-ethylene process allows comparison among them because it is an economic assessment of the annualized total cost to build and operate a bio-ethylene plant divided by the total annual bio-ethylene production.^{35,47}) The processes are: sugar-canederived ethanol to ethylene, with and without bio-energy, with carbon capture and storage (BECCS); bio-methanol to olefin; and conventional steam cracking of naphtha, which was defined as the benchmark route for comparison.

The next section of this article shows the current state of the Brazilian chemical industry, aiming to demonstrate its current lack of competitiveness. The paper goes on to describe the methodology applied to assess the levelized costs of ethylene from naphtha, ethanol, and bio-methanol, and the methods used for the sensitivity analysis. It then presents the break-even carbon prices of the selected routes, the results of the sensitivity analysis and the discussion of the final results.

Brazil's chemical industry

The Brazilian industry's share in the country's GDP has been decreasing since the early 1990s.^{48–50} This process is also happening in some developed economies,⁵¹ but the deindustrialization process in Brazil took place at an early stage in the country's development,⁴⁹ when Brazil's per capita income was much lower than in the developed countries.⁵¹ Moreover, this process has occurred in a country with a population with a low level of schooling and an economy where, instead of the tertiary sector expanding, the primary sector dominates.

Aside from deindustrialization, Brazil has suffered from a deep economic recession and political crisis, losing competitiveness in the international market. According to the World Economic Forum (2018),⁵² in 2017, the country reached the worst position of the past 10 years in global competitiveness ranking, and its industrial production fell back to 2004 levels. This compromises economic growth and affects the generation of jobs and income.

The chemical industry is one of the more successful integrated industrial sectors in Brazil.⁵³ Nevertheless, the country has increased its dependence on imported chemicals. This trend may be reinforced over the next few decades, especially due to the lack of recent investment (Fig. 1), including the announcement by the Brazilian state-controlled company, Petrobras, that it was cancelling expansion plans.⁵⁴

In 2017, the Brazilian chemical industry accounted for 10% of country's industrial GDP⁴³ but its turnover dropped from sixth to eighth position worldwide. To retake its position, Brazil's chemical sector is betting on the removal of several barriers that affect its competitiveness: high costs of feedstock, excessive bureaucracy, high price of electricity, and high logistic costs.⁴³ This study focuses on one of these barriers: the high costs of feedstock. Brazil's petrochemical industrial facilities face some of the highest naphtha prices in the world.⁴³ Domestic natural gas is expensive and is associated with the offshore production of crude oil.⁴³

In summary, taking into account the strong influence that divestment in the chemical industry has had on the Brazilian economy, the sector has to reinvent itself to be able to compete as a global player. In this regard, the Brazilian chemical sector could consider its comparative advantages, such as the low cost of sugarcane, which has



Figure 1. Investments in Brazilian chemical industry. Source: Based on Deloitte.43

already encouraged the production of bioethanol for the production of ethylene. Since 2010, BRASKEM has operated a commercial plant with a production capacity of 200 kt per year of polyethylene from bio-ethylene.⁵⁵ Under current market conditions, ethylene from ethanol would not compete with ethylene from naphtha or natural gas, simply because ethanol prices tend to follow the price of gasoline.^{56–58} Petrochemical naphtha is less expensive than gasoline but the same applies to ethane from natural gas (particularly for stranded reserves).⁵⁹ This study therefore assesses whether bio-ethylene has an environmental advantage (expressed as lower CO₂ emissions than ethylene derived from fossil fuel), and whether those emissions, if valued (or priced), could generate a financial advantage for this product. This could also be seen as an economic benefit from mitigating CO_2 emissions in the Brazilian chemical sector.

Methods

The selected routes to ethylene production assessed by this study were conventional steam cracking of naphtha, ethanol to ethylene (with and without BECCS), and bio-methanol to olefins (methanol to olefins, or MTO) representing the current most promising routes for ethylene production from biomass. The estimated levelized costs (LC) and GHG emissions intensity of these bio-production routes were compared with their fossil fuel counterpart. The GHG emissions intensity of each route was assessed from cradle to gate, calculated using a mass-based allocation method. (Allocation can be done according to the relative mass, volume, energy, or economic value of the products and coproducts. This study has adopted a mass-based allocation; the environmental impact is therefore distributed between the outputs based on mass.) To find the break-even carbon price of these bio-products, the LCs were subject to a range of different carbon prices (from US\$0 to US\$220/tCO₂).

The LCs calculated for each route are given in Eqn (1).

$$LC_{i} = \frac{CAPEX_{i} + FOM_{i} + VOM_{i}}{PRODUCTION_{i}} \pm CARBON_{i}$$
(1)

where,

 LC_i = levelized costs of route i (\$ t⁻¹ ethylene);

i = ethylene route;

 $CAPEX_i$ = annualized capital expenditure for route *i* (\$ year⁻¹); FOM_i = fixed operations and maintenance costs for route *i* (\$ year⁻¹);

 VOM_i = variable operations and maintenances costs for route *i* (\$ year⁻¹);

FEEDSTOCK_i = costs with feedstocks for route *i* (\$ year⁻¹); *REVENUE_i* = by-products revenues for route *i* (\$ year⁻¹); *PRODUCTION_i* = total production of route *i* (t ethylene year⁻¹); *CARBON_i* = CO₂ emissions costs or revenue for route *i* (\$ t ethylene⁻¹), calculated accordingly to Eqn (2):

$$CARBON_i = annual \ emissions_i \times carbon \ price$$
(2)

where,

Annual emissions_i = annual CO₂eq emissions from route i (tCO₂eq t ethylene⁻¹);

Carbon price = carbon price ($t CO_2 eq^{-1}$).

Table 1 shows the assumptions for the LC costs for the overall routes.

Primary data for capital expenditure (CAPEX) and operating expenses (OPEX) for the processes assessed by this study were adjusted to US\$ $_{2017}$, according to the Chemical Engineering Plant Cost Index (CEPCI).⁶³

Assessment of ethylene production routes

This study compared three ethylene production routes: sugarcane-derived ethanol to ethylene, bio-methanol to olefin (using sugarcane bagasse as feedstock), and conventional steam cracking of naphtha. For the first option, there is already a plant of 200 kt/year installed in Brazil.⁵⁴ It is based on a simple, established process, whose main advantage is the large Brazilian sugar cane industry, but whose drawback is the cost of ethanol supply. The second route was also based on a by-product of the sugar cane industry, i.e. bagasse. It is less expensive than ethanol but its conversion requires a more complex process. Finally, the fossil-fuel route based on naphtha was selected because it is the major process adopted in Brazil⁵⁴ and even in China, which is globally the major importer of petrochemicals and a potential market for exports from Brazil.

Before detailing the routes, it is worth noting that the emission factor of each process depends on the final disposal of the final product (ethylene into its derivative). For instance, if the bio-ethylene is converted into polyethylene plastic

| Table 1. Economic assumptions. | |
|--|-----------|
| Annual discount rate ^a | 9.8% |
| Economic lifetime ^a | 30 years |
| Base-year | 2017 |
| Exchange rate ^b | 1.13 €/\$ |
| ^a It was assumed that 10% of the investment was financed at a 15% annual interest rate ⁶⁰ and 90% from the Brazilian public development bank, BNDES, at a 8.5% annual interest rate (BNDES, 2017). ⁶¹ | |

^bAverage exchange rate from Statista for 2017.⁶²

bag, which is a single-use product, it can be incinerated, recycled, or landfilled at the end of life. Each one of these final disposals generates GHG emissions. However, the ethylene product could be converted into long life-time products, as a strategy of carbon sink. In this case, if all the carbon embodied in 1 t of bio-ethylene is considered as biogenic carbon storage 3.14 tCO₂ would need to be subtracted from the bio-ethylene's total life-cycle GHG emissions. (The molar mass of ethylene (C_2H_4) and carbon dioxide (CO_2) is 28 gmol/g and 44 gmol/g, respectively. Stoichiometrically, if burned, one molecule of ethylene emits two molecules of CO_2 , i.e., 3.14g CO_2 / g ethylene (2 × 44 / 28).)

This article does not detail the assessment of the final disposal, but this step is crucial for understanding the real benefits of bio-based routes. This study therefore assessed a best case for the bio-ethylene products' final disposal (Table 2), which means that the biogenic carbon captured in the sugarcane production is embodied into a long-lifetime product, and a worst case for the bio-ethylene products' final disposal, when the biogenic carbon is fully released in the atmosphere at the end of their life.

For the best case of bio-ethylene products' final disposal, this paper considers bio-plastics as construction material, such as façade panels, windows, or water pipes.⁶⁴ In Brazil, the construction industry was the largest consumer of plastics in 2017, followed by the food industry, accounting for 23.8%⁶⁵ and 20.2%,⁶⁶ respectively.

Steam cracking of naphtha

Steam cracking of naphtha is the dominant technology for the production of light olefins, followed by ethane steam cracker, representing 40% and 38%, respectively, of global production in 2017.^{59, 67} In Brazil, naphtha represents 92% of petrochemical feedstock and Petrobras is practically the only naphtha and natural gas producer in the country, meeting part of the national demand with its own production and with imports.⁵⁴ This process is energy intensive (60% of energy required in the ethylene production plant is consumed in the cracker) and it is responsible for high CO₂ emissions.^{68, 69}(Different allocation methods influence the final CO₂ emissions of a process that outputs various co-products. Still, the scientific literature agrees with the high CO₂ emission intensity of ethylene production, ranging from a minimum value, according to which emissions

| Table 2. Carbon dioxide emission range fromfinal disposal of bio-ethylene. | | |
|--|--|---|
| Olefin | Worst case (t CO ₂ / t ethylene) | Best case (t CO ₂ / t ethylene) |
| Bio-ethylene | 0 | -3.14 |

are allocated for each co-products according to mass or energy, to a maximum value, according to which emissions are allocated solely to the main product.)

This process produces mostly ethylene (32% by mass, on average) but also propylene, butadiene, aromatics – the so-called high-value chemicals (HVCs) – pyrolysis gasoline, and fuel-grade by-products, such as hydrogen and methane used to fuel the process or to be exported.^{15, 16} Table 3 shows the yields on a mass basis for each HVC considered in this route. The cost data for a naphtha steam cracker is presented in Table 4.

The route from naphtha to ethylene was assessed on a cradle-to-gate basis (Fig. 2). The starting point of the lifecycle analysis is the emissions from the upstream operation of oil and gas production accounting for 21.60 Mt CO_2 eq. in 2017,⁷³ when 130.55 Mt of oil were produced.⁷⁴ The distance from the well to refinery was assumed to be 50 km.

Table 3. High-value chemical yields of naphtha steam cracker.

| High-value chemicals | Yield (wt%) |
|----------------------|-------------|
| Ethylene | 0.32 |
| Propylene | 0.17 |
| C4 ^a | 0.13 |
| BTX ^b | 0.104 |

^aC4 cracking fractions are the mixture of butane, and butadiene. ^bMixture of benzene, toluene, and xylene. Source: Ren *et al.*¹⁶

| Table 4. Cost data for a naphtha steam cracker. | | |
|--|---------|--|
| Capacity (Mt/y) ^a | 0.50 | |
| Capacity factor (%) | 0.90 | |
| Ethylene prod. (Mt/y) | 0.45 | |
| Propylene prod. (Mt/y) | 0.24 | |
| C4 prod. (Mt/y) | 0.18 | |
| BTX prod. (Mt/y) | 0.14 | |
| CAPEX (M\$ ₂₀₁₇ /y) ^b | 147.68 | |
| FOM (M\$ ₂₀₁₇ /y) ^c | 56.03 | |
| VOM (M\$ ₂₀₁₇ /y) ^d | 761.71 | |
| Propylene price (\$ ₂₀₁₇ /t) ^e | 766.67 | |
| Butadiene price (\$2017/t) ^e | 1002.92 | |
| BTX price (\$ ₂₀₁₇ /t) ^e | 751.67 | |
| Naphtha prices (\$ ₂₀₁₇ /t) ^f | 541.00 | |
| ^a The plant capacity is the average capacity of naphtha steam crackers in Brazil (OGJ, 2015). ⁴⁵ ^b From TNO estimates based on market prices (2016). ⁷⁰ ^c Fixed operation and maintenance (O&M) costs from Ren <i>et al.</i> (2006). ¹⁵ ^d Variable operation and maintenance (O&M) costs includes the | | |

^eFrom INTRATEC.⁷¹ ^fFrom COMEXSTAT.⁷²



Figure 2. Life-cycle system boundaries for naphtha steam cracking route.

The assumed pipeline distance from well to refinery is conservative. For instance, the distance of the pipeline that connects the Ilha d'Água Oil Terminal to the Refinaria Duque de Caxias (REDUC) refinery, both in Rio de Janeiro, is 14km, whereas the pipeline distance from Barueri oil terminal to refinery Refinaria de Paulínea (REPLAN) refinery, both in São Paulo, is 50 km.⁷⁵

The oil transportation was based on pipelines with an electricity consumption of 1.51 kWh/bbl.76 The electricity is assumed to be purchased from the grid with an emission factor of 0.0927 kg CO₂/kWh.⁷⁷ Emissions from oil refining totaled 22.8 MtCO2 eq. in 201773 for the 87 Mt of oil processed.⁷⁴ The total amount of oil products obtained from oil in Brazilian refineries in 2017 reached 84.6 Mt, with naphtha representing 2.5% of total output. This small fraction of naphtha is explained by the fact that fuel prices in the 2011-2014 period were controlled by the Brazilian government. This kept fuel prices below international parity to prevent inflation and led to an increase in the country's gasoline demand.^{78, 79} To attend this growing gasoline demand, unfinished naphtha, from Brazilian refineries, was blended into the gasoline pool, decreasing supply for the petrochemical sector. This study sought to fix that distortion by using the average mass yield of naphtha from 2007 to 2017, which corresponds to 4.8%.⁷⁴

The distance for the transportation of naphtha from the refinery to the petrochemical industry was also assumed to be 50 km and made through pipelines.⁷⁶ For the steam-cracking process a mass yield of ethylene/HVC of 0.48 and an emission factor of 0.66 tCO₂/t ethylene⁴⁴ were assumed.

Table 5 indicates the emission factor calculated for this route. The final number is in accordance with the emission factor proposed by Simapro software version 8.5.2.0 (1.13 t CO_2eq/t ethylene).

Ethanol to ethylene

Ethylene was made from dehydration of ethanol until the expansion of the petrochemical industry in the mid-1940s, when ethylene started to be produced from thermal cracking of hydrocarbons.^{80, 81} The costs assumed for the ethanol-based route were derived from a simulation using Aspen Plus[®] software, v. 10, detailed in Secchi *et al.*,⁸² based on a real Brazilian ethanol-to-ethylene plant. The plant was simulated with a capacity of 200 kt per year, which corresponds to the capacity of the bio-ethylene plant in Brazil. However, this study adopted a capacity of 500 kt per year of ethylene to be consistent with the naphtha steam cracking plant that was also assessed. The costs (Table 6) were calculated using a scaling coefficient of 0.6258.⁸³ Again, the system was assessed from cradle-to-gate (Fig. 3).

The production of bioethanol from sugarcane has been reported many times in the literature.^{84–88} The main products from processing sugarcane are ethanol, bagasse for

Table 5. Greenhouse gas emissions for naphtha

| steam cracking. | |
|------------------|---------------------------------|
| Step | tCO ₂ eq/ t ethylene |
| Upstream | 0.01 |
| Transportation 1 | 1.72×10 ⁻⁷ |
| Refinery | 0.36 |
| Transportation 2 | 3.55 x 10 ^{−6} |
| Steam cracking | 0.66 |
| Total | 1.02 |
| | |

| Table 6. Costs for the ethanol to ethylene route. | | |
|--|--------|--|
| Capacity (kt/y) ^a | 500.00 | |
| Capacity factor | 0.90 | |
| CAPEX (M\$ ₂₀₁₇ /y) ^a | 44.09 | |
| OPEX (M\$ ₂₀₁₇ /y) ^a | 75.29 | |
| Ethanol costs (M\$ ₂₀₁₇ /y) ^b | 517.89 | |
| Ethanol price (\$2017/t) ^b | 661.42 | |
| ^a Based on Secchi <i>et al</i> . ⁸² ^b From INTRATEC. ⁷¹ | | |

cogeneration (of electricity and steam), and electricity for the grid (from surplus bagasse). The first step in this whole-of-life system is the cultivation of sugarcane (Table 7).

The emission factor for ethanol production is 2.6 g CO₂ eq/ MJ ethanol and the bagasse for cogeneration yield is 8.7 kg/t cane, according to Seabra *et al.*⁸⁶ The possibility of carbon capture from ethanol fermentation was also considered. It is a commercially proven technology with low specific costs (US\$11/t CO₂).⁴⁷ Ethanol production is an important opportunity for BECCS deployment. Actually, most current



Figure 3. Life-cycle system boundaries for the ethanol to ethylene route.

| Table 7. GITG ethissions for sugarcane | |
|--|--|
| cultivation. ^a | |

| Sugarcane cultivation steps | EF (gCO ₂ eq/MJ ETOH) |
|-----------------------------|----------------------------------|
| Sugarcane farming | 6.8 |
| Field emissions | 6.7 |
| Agricultural input | 3.8 |
| Sugarcane transportation | 1.4 |

^aSugarcane trash burning in Brazil will be completely phased out by 2021 to meet State Law N° 11.241/2002. The emissions from this step were therefore not included in this LCA.^{89, 90} Source: Seabra *et al*.⁸⁶ BECCS projects use CO₂ captured from ethanol production as input for enhanced oil recovery.^{19, 47, 91, 92}

A distance of $50 \text{ km}^{20, 93}$ to transport by truck from the ethanol distillery to the dehydration plant was assumed. The specific consumption of diesel is $0.020 \text{ L/t.km}^{76}$ and the emission factor for diesel combustion is $75.243 \text{ kg CO}_2 \text{ eq/TJ.}^{94}$

The specific energy consumption of the ethanol dehydration step was set as 0.04 GJ (natural gas)/t ethylene.⁹⁵ The emission factor of natural gas is 0.056 t CO_2/GJ .⁹⁴ Finally, as mentioned before, the 'best case' of bio-ethylene final disposal captures 3.14 t $\text{CO}_2/$ t ethylene, whereas the 'worst case' does not capture biogenic CO_2 .

Table 8 summarizes the emission factor calculated for this route. It is worth noting that the GHG emissions presented in Table 8 were converted from tCO_2eq/t ethanol to tCO_2eq/t ethylene by a mass-based allocation.

Methanol to olefins

Finally, this study also assessed the methanol to olefins (MTO) route. In this case, methanol is produced via syngas from gasification of sugarcane bagasse.^{96, 97} The bio-methanol is then used as a feedstock to produce ethylene and propylene in a ratio between 0.5 and 1.5 to 1.⁹⁸ In this study, ethylene was assumed to be the main product, and propylene as the byproduct. Table 9 summarizes the costs for this route. Again, the system was assessed from cradle to gate (Fig. 4).

The sugarcane cultivation step is the same as the one used in the ethanol-to-ethylene route. However, in this case, the surplus of bagasse that would be sold to thermoelectric plants to generate electricity for the grid is, instead, used for methanol production via syngas. The mass yield bagasse / total products is 0.024.⁸⁶ (The total products of the distillery is assumed to be ethanol, bagasse for cogeneration, and bagasse

| Table 8. GHG emissions for the ethanol-to- ethylene route. | | |
|---|--------------------------------------|--|
| Steps | EF (t CO ₂ eq/t ethylene) | |
| Сгор | 0.04 | |
| Ethanol production | 0.12 | |
| Ethanol production with BECCS | -0.45 | |
| Transportation | 0.00 ^a | |
| Dehydration | 0.00 ^b | |
| Total | 0.17 | |
| Total with BECCS | -0.41 | |
| Final disposal ('best case') | -3.14 | |
| Final disposal ('worst case') | 0.00 | |
| ^a Transport by truck emits 0.0046 t CO ₂ /t ethylene. | | |

^bDehydration process emits 0.0022t CO₂/t ethylene.

| Table 9. Costs for MTO route. | | |
|--|--------|--|
| Capacity (kt/year) | 500.00 | |
| Capacity factor | 0.90 | |
| Ethylene/propylene ^a | 0.90 | |
| CAPEX (M\$ ₂₀₁₇ /year) ^b | 73.00 | |
| OPEX (M\$ ₂₀₁₇ /year) ^b | 3.57 | |
| Price propylene (\$/t) ^c | 766.67 | |
| Methanol/HVC ^{2d} | 2.70 | |
| Price bio-methanol (\$/t) ^e | 380.00 | |
| ^a Rasod on American of al ⁹⁹ | | |

^bFrom TNO estimates based on market prices (2016).⁷⁰

^cFrom INTRATEC (2019).⁷¹

^dFrom Huisman et al.¹⁰⁰

^eFrom TNO estimates based on market prices (2016).⁷⁰ The high valued chemical here is the mixture of ethylene and propylene.



Figure 4. Life-cycle system boundaries for MTO route (feedstock: Sugarcane bagasse). Note: WGS = water gas shift.

surplus for methanol production.) Trucks transport the bagasse for an assumed 50 km distance, from the distillery to the gasification and methanol synthesis plants. Diesel specific consumption is 0.020 L/t.km,⁷⁶ with an emission factor of 75.243 kg CO₂ eq/TJ.⁹⁴

The emission factor for the gasification and methanol synthesis steps is $1.83 \text{ t CO}_2/\text{t}$ methanol,⁹⁶ including electricity and steam consumption, and process emissions. The electricity consumption is 0.093 kWh/ t methanol,⁹⁶ and steam consumption is 0.00173 t/ t methanol.⁹⁶ After the

| Table 10. GHG emissions for MTO route. | | |
|---|--------------------------------------|--|
| Step | EF (t CO ₂ eq/t ethylene) | |
| Сгор | 0.08 | |
| Transportation | 0.01 | |
| Gasification, WGS, CO ₂ removal, | 0.23 | |
| methanol synthesis | | |
| МТО | 0.10 | |
| Total | 0.42 | |
| Final disposal ('best case') | -3.14 | |
| Final disposal ('worst case') | 0.00 | |

gasification, a water-gas shift (WGS) reaction is used to adjust the H2:CO ratio in the syngas by converting CO and steam into H₂ and CO₂.^{20, 96, 101} Carbon dioxide is removed with a capture rate of 95%.²⁰ The MTO process emission factor is 0.10 tCO₂/t ethylene according to Liptow *et al.*¹⁰² The 'best case' of final disposal for this route captures 3.14t CO₂/t ethylene, whereas the 'worst case' does not capture biogenic CO₂. Table 10 indicates the emission factors for this route.

Sensitivity analysis

The price of feedstock influences the variable operating costs of the processes assessed. A sensitivity analysis was therefore performed on the naphtha, ethanol, and bagasse prices. For this purpose, an uncertainty range of -50% to 100% was applied to the feedstock prices. Market feedstock prices were based on INTRATEC⁷¹ and COMEXSTAT.⁷² It should be noted that a variation in the naphtha price also affects the prices of steam-cracking by-products.

A sensitivity analysis on bio-based plants' CAPEX was also conducted. Economic analysis tends to underestimate the capital costs and overestimate the plant performance if compared with values observed for a first-of-a-kind (pioneer) plant.¹⁰³ An uncertainty range of -50% to 100% was therefore applied to the CAPEX of both bio-based ethylene processes.

The break-even carbon prices were calculated subject to variations in relative prices of the feedstocks (naphtha / ethanol and naphtha / bagasse) and in the CAPEX of both bio-based plants. Break-even carbon prices allow the levelized costs of bio-based and fossil ethylene to be equal. This study applied the Solver optimization tool in Microsoft Excel to determine how the desired break-even prices could be achieved by changing the feedstock prices for each of the selected routes and by ranging the bio-based plants' CAPEX. It should be noted that the sensitivity analysis was assessed assuming only the 'best case' for ethylene final disposal, i.e., its conversion into long life-time products.

Results and discussion

Break-even CO₂ prices for the worst and best cases of ethylene final disposal

Figure 5 presents the results of the modeled routes for the 'worst case' final disposal. When the biogenic carbon capture is not considered in the bio-ethylene's life-cycle GHG emissions, the break-even carbon prices are extremely high: US\$241/ t CO_2 , US\$384/ t CO_2 , and US\$645/ t CO_2 for the ethanol-to-ethylene route with BECCS, ethanol to ethylene without BECCS, and bio-methanol to ethylene, respectively. Moreover, the bio-based ethylene routes' behavior in this situation shows that the higher the carbon price the more costly these routes become, except for the ethanol-to-ethylene route with BECCS, which already presents a negative lifecycle emission, as shown in Table 8.

Figure 6 shows the results for the 'best case' final disposal. The lines with a negative slope correspond to the routes to produce ethylene using biomass as feedstock. This behavior is explained by their capacity to generate negative emissions: the higher the carbon price the cheaper these routes become. For instance, for a carbon price of US\$120/ tCO₂, the costs

associated with the ethanol-to-ethylene route with BECCS, the ethanol-to-ethylene route without BECCS, and the biomethanol-to-ethylene route decrease to US\$1.006, US\$1.060, and US\$1.156/ t ethylene, respectively. This means that, even though the bio-based routes are more costly, the cost becomes lower than their fossil counterparts when the external cost of emitting CO₂ to the atmosphere through a carbon prices is taken into account. In other words, the revenue derived from CO₂ emissions abatement (quantity times price) more than compensates for the higher producer costs from biomass. In the end, the CO₂ break-even prices (which equalize bioroutes costs with naphtha route costs) are US\$75/ t CO₂ for the ethanol-to-ethylene route with BECCS, uS\$82/ t CO₂ for the ethanol-to-ethylene route without BECCS, and US\$106/ t CO₂ for the bio-methanol-to-ethylene route.

As the feedstock cost accounts for 70% of the total production costs of bio-ethylene in the ethanol-to-ethylene route, this could give Brazil's chemical industry a competitive advantage. Moreover, the production of ethanol from sugarcane in Brazil produces bagasse as a residue that can be sold for electricity generation or, in the case of this study, to produce bio-ethylene. Appropriate use of bagasse could therefore improve the economics of the sugarcane ethanol









production in Brazil. For instance, a dedicated facility using the sugarcane ethanol-to-ethylene process and converting the surplus bagasse into olefins through MTO would output 0.04t of ethylene per tonnes of sugarcane, with an average levelized cost of US\$1435.64/ t ethylene (based on weighting the share of each product from each route), and an average CO₂ break-even cost of \$86/ t CO₂.

During COP 21, Brazil announced the target of reducing GHG emissions by 37% compared to 2005 levels by 2025, and the intention to reduce emissions by 43% by 2030.¹⁰⁴ In the recent past, the country considered the use of market mechanisms to reduce GHG emissions, as presented in its Nationally Determined Contribution.^{105, 106} However, there is no clear indication of how these instruments will be used.¹⁰⁴ It signals that long-term investments need to be made in order to decarbonize the economy.^{107–109} This paper does not aim to discuss the design of a carbon pricing instrument for Brazil but instead it shows that a local or a global CO₂ market could boost the use of abundant primary energy sources in Brazil to produce ethylene. Moreover, it shows that, under a carbon pricing mechanism, the bio-based chemical industry, based on sugarcane, could produce ethylene competitively when compared to the alternative process from naphtha.

The hypothesis tested in this study was that the Brazilian petrochemical industry could benefit from a leadership in cost through a bio-ethylene quality premium, and this could favor an industry in a severe crisis.

In other words, there would be a co-benefit for Brazil to mitigate CO_2 emissions in the chemical sector, expressed in terms of competitiveness gains, if the CO_2 abated is priced and the ethylene produced is used in long life-time materials. The range of carbon prices available in the literature^{110–112} to keep global temperatures within the desired limit of 2°C (\$ 162–505 per tCO₂) is higher than the range of bio-ethylene break-even prices found in this study for the 'best case' (\$ 75–106 per tCO₂). Nevertheless, the break-even prices found here are still above the price found in carbon markets already established globally.¹¹³

Sensitivity analyses

Table 11 shows the break-even CO_2 prices associated with the variation in the relative prices of feedstocks (naphtha / ethanol and naphtha / bagasse) for the best case of final ethylene disposal. As the relative feedstock prices increase, the break-even price for the bio-methanol-to-ethylene route becomes lower than that for the ethanol-to-ethylene route. This result was expected because the ethanol-to-ethylene process is more sensitive to a variation in feedstock price. Instead, a reduction in the relative prices can make the bio-ethylene feasible without the need for pricing the CO_2 (when the break-even

| Table 11. Break-even CO ₂ prices across a range in relative feedstock prices. | | |
|--|---|--|
| Feedstock relative price variation | Break-even CO ₂ price in US\$/t ethylene (from ethanol) | Break-even CO ₂ price in US\$/t ethylene (from bio-methanol) |
| -50% | -61.80 | -9.70 |
| -25% | 10.20 | 47.98 |
| 0% | 82.20 | 105.68 |
| 25% | 154.20 | 163.37 |
| 50% | 226.20 | 221.05 |
| 75% | 298.21 | 278.74 |
| 100% | 370.21 | 336.43 |

Table 12. Break-even CO₂ prices across a range in bio-based plants' CAPEX.

| CAPEX variation | Break-even CO ₂ price in US\$/t ethylene (from ethanol) | Break-even CO ₂ price in US\$/t ethylene (from bio-methanol) |
|--------------------|--|--|
| -50% | 69.94 | 84.08 |
| -25% | 63.81 | 73.28 |
| 0% | 82.20 | 105.68 |
| 25% | 88.33 | 116.48 |
| 50% | 94.46 | 127.28 |
| 75% | 100.59 | 138.08 |
| 100% | 106.73 | 148.88 |

 $\rm CO_2$ price is negative). This can happen sometimes, especially just before the driving season in the USA (starting from May–June) when the price of gasoline (and, thus, the price of naphtha) increases,¹¹⁴ and when the sugarcane supply season starts in Brazil.¹¹⁵

Table 12 shows the break-even CO_2 prices associated with the variation in bio-based plants' CAPEX. It is expected that pioneer (first-of-a kind) plants will face higher costs than n^{th}_{-} of-a-kind plants,¹⁰³ meaning that it is wise to consider a conservative break-even CO_2 price range of 100–150 US\$/ t CO_2 for implementing a strategy aiming at producing bioethylene from sugar cane in Brazil. This range might decrease due to learning effects and yield increases as the strategy consolidates.

Conclusions

Our findings indicate that bio-ethylene from sugar cane could become competitive with naphtha-derived ethylene for a price range of around 75–150 US\$/tCO₂, depending on whether the ethylene is converted into long life-time products

and the costs of pioneer plants. This competitiveness would be represented by both the revenues generated from carbon credits, and by the attractiveness to investors searching for regions with available, cheap, and renewable feedstock.

Bio-based chemicals could be an important step in the transition to a sustainable economy. From a technical point of view, the proposed transition could be closer than expected; however, the geopolitical situation and economic aspects, such as feedstock prices, are unstable market factors that make any assessment uncertain.¹⁸ The production costs estimated in this study therefore depend not only on the future carbon prices but also on the prices of crude oil, sugar, fuels, and feedstocks. Moreover, first-of-a-kind plants always present high project and process contingencies and need learning to improve competitiveness.

The uncertainty of our results also stems from the LCA approach. Even though this study is based on a cradle-to-gate analysis, the disposal of ethylene products is crucial for an understanding of the real benefits of producing bio-ethylene for the Brazilian chemical industry. The final disposal of ethylene was therefore assessed in a simplified manner in this case, looking at the 'best case' and the 'worst case' final disposal for the bio-based routes, i.e., the final product is transformed into a long long life-time product, or it is incinerated, emitting the total amount of biogenic carbon captured during sugarcane production. The GHG emissions of bio-based chemicals also vary across a wide range of values, due to the multiplicity of methodological choices regarding allocation procedures, system boundaries and functional units, and assumptions made in the LCA studies that were reviewed.^{81,84,95,96,99,102,116,117}

For this reason, a comparison between our results and others found in the literature is difficult and calls for a more uniform procedure. With regard to the LCA uncertainties, the present study did not consider the emissions from land-use change for ethanol production. The reason behind this approach is that the expansion of sugarcane area will hardly cause indirect deforestation in the Brazilian Amazon rain forest.^{86, 88} Studies based on satellite images show that the deforestation due to sugarcane expansion from 2005 to 2008 was around 0.18 Mha.¹¹⁸ This slight indirect impact can be explained by livestock intensification, expansion of sugarcane over pasture areas, and improvement in the yields of different crops.⁸⁸ Besides, the forecast ethanol demand in the coming 15 years will require no more than 6 Mha¹¹⁹ of the 64 Mha suitable for sugarcane production.¹²⁰

The sensitivity analysis performed in this study shows that the ethanol-to-ethylene route is more sensitive to a variation in feedstock price (ethanol price) than the other routes selected. It is worth noting that the price of bagasse used in this study is low because it is a residue from ethanol production. In future, the bagasse price may increase with an increase in demand for it. The sensitivity analysis also shows that, if that occurs, the break-even price for the biomethanol-to-ethylene route is lower than for the ethanol-toethylene route.

Further studies should also evaluate other feedstocks for the production of ethylene, such as alternative sources of biomass besides bagasse. They could also assess the methanol production from the hydrogenation of CO_2 with H_2 being produced through water electrolysis.

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Camilla C.N. de Oliveira

Camilla C.N. de Oliveira is a researcher and a PhD candidate in energy planning at the Federal University of Rio de Janeiro (COPPE/UFRJ). She is a chemical engineer and holds an MSc in energy planning. Her research interests focus on the non-energy use of oil and biomass in energy transition

scenarios, climate change, and energy system analysis.



Pedro R.R. Rochedo

Pedro Rochedo is a professor at COPPE/UFRJ and holds a PhD in energy planning. He has a bachelor's degree in chemical engineering. His research interests include energy system analysis, integrated assessment modelling, and climate change.



Rajat Bhardwaj is a research scientist with background in chemical engineering at TNO, Netherlands. In this role, Rajat works on creating roadmaps for reducing the CO_2 emissions along with companies and industrial clusters in the Netherlands. The prime motivation is in realizing

opportunities for developing and integrating technologies, aimed to maximize the use of existing infrastructure and provide long term license to operate with minimal costs. Rajat is leading technology development for new innovative low carbon technologies such as methane pyrolysis within the energy transition unit at TNO.



Ernst Worrell

Ernst Worrell is professor of energy, resources and technological change at Utrecht University, The Netherlands. Previously, he worked at Lawrence Berkeley National Laboratory and Princeton University. His research focuses on energy and material

efficiency, and the role of technological change in the development of future energy and resource systems.



Alexandre Szklo

Alexandre Szklo is an associate professor of the energy planning program of COPPE at the Federal University of Rio de Janeiro (UFRJ). He obtained his PhD from COPPE / UFRJ, and is a chemical engineer. Alexandre is the author of numerous books and

papers in scientific journals, and has supervised more than 120 doctoral theses and master's dissertations.