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A short-cut model for predicting biomethane availability after biogas upgrading

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ABSTRACT

Biomethane increasingly grows in importance in the bioenergy sector, as it is a renewable energy source that promotes waste recovery and GHG (greenhouse gases) reduction. In Brazil, the legal framework for biogas and biomethane is being developed, especially in the State of São Paulo. However, many of the final uses to biomethane require an upgrading and cleaning process, to remove contaminants such as H_2S and CO_2. Facing the great number of technological options to promote biogas upgrading and cleaning so far, policymakers and energy planners might lack the tools to accurately and readily estimate biomethane potentials to comply with a given biomethane quality standard. Our main objective thus is to propose a short-cut, mass balance-based model to predict biomethane availability after promoting a biogas cleaning and upgrading process, regardless of the source of organic feedstock. The model development results in the ratio of biogas to biomethane production and other relevant parameters regarding biomethane use, such as its LHV. The correlation with data from the literature shows that the model has a satisfactory prediction, even when using upgrading technologies that have high methane losses. The model was applied to a case study of upgrading biogas from vinasse from ethanol production in the state of São Paulo; it aided in choosing the upgrading technology for biogas focusing on biomethane injection in the natural gas pipeline and in replacing diesel oil in trucks and heavy-duty machinery in the ethanol plant. Using the proposed model, it was estimated that 1.975×10^9 Nm^3/y of biomethane could be produced, supplying 16.6% of the NG consumption in the State of São Paulo and making it possible to displace the entire diesel oil consumption in ethanol mills. The use of biomethane in the ethanol plants of São Paulo would avoid 3.965×10^6 t_{CO2eq} of GHG emissions, which represents 5.48% of the GHG emissions of the state in 2016.

1. Introduction

The production of biofuels from biomass and waste instead of using these sources "as is" for energy purposes is an interesting approach to achieve cleaner production principles, such as reduction of overall greenhouse gases (GHG) emissions, waste recovery and reduction of environmental impacts (Kurnia et al., 2016; Leme and Seabra, 2017). In that sense, the use of biogas produced from wastewater anaerobic digestion and landfills, as well as other organic residues, is aligned with cleaner production goals.

There are different options for inserting biogas in the energy sector. One is the use of raw biogas for combined heat and power production (CHP), which requires a simple prior cleaning step to remove contaminants that could damage the equipment, such as H_2S and siloxanes. This option is suitable for distributed generation and the conversion technologies can be, for example, internal combustion engines and gas micro turbines (Santos et al., 2016). The other alternative is the upgrading of biogas to biomethane, which can be used as a fuel for transportation, being a renewable option in places where vehicular fuel is limited (Larsson et al., 2016). Biomethane as a vehicle fuel is already a reality, especially in Sweden, where its development was influenced by policy instruments and could potentially reduce GHG emissions in transport by 25% (Olsson and Fallde, 2015).

The use of biomethane as a biofuel is already a reality in Europe, mostly backed up by the Europe 2020 policy, as a means of displacing fossil fuels and reducing CO_2 emissions (Frank et al., 2013). However, in Brazil, biomethane is still an emerging source of

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energy. Data from CIBIOGAS (International Centre for Renewable Energy-Biogas) shows that there are currently 155 biogas plants in Brazil, most of them producing biogas from animal residues and industrial and agro-industrial wastes for its own heat or power needs (CIBIOGAS, 2018). Considering the size of Brazil and the size of its population (which is closely related to the generation of waste), this figure reveals a small use of the biogas and biomethane potential in the country. For instance, data from IEA reveals that European countries with smaller populations present a much larger number of biogas plants: Germany has 10,212 plants, while having only 39.8% of the population of Brazil, and the United Kingdom has 913 plants, while having 31.6% the population of Brazil (IEA, 2017). Data from the Brazilian National Agency of Electric Energy (ANEEL) also reveals that biogas is responsible for only 0.08% of the total installed power for electricity generation in Brazil (ANEEL, 2018), which corroborates the fact that biogas and biomethane are still emerging sources of bioenergy in Brazil. Particularly, according to Joppert et al. (2018), the State of São Paulo is ahead of the other federative units of Brazil in terms of legislation and regulation regarding biomethane. The state has its own biogas incentive plan ("Plano Paulista de Biogás"), includes biogas as a renewable energy source in it energy planning ("Programa Paulista de Energia – 2020") and the energy regulating agency of the state of São Paulo (ARSESP) has already developed regulation for biomethane injection in the gas pipelines (ARSESP Deliberation 744). Additionally, the authors cite the new National Policy of Bioenergy (RENOVABIO) and the initiatives of private and civil society associations such as ABIOGAS and CIBIOGAS as supporting facts to the development of the biogas and biomethane market in São Paulo.

These biofuels are, however, important sources of bioenergy to help Brazil meet the National Contribution (NDC) signed by Brazil in the Paris Agreement, the main objectives of which require a 37% reduction in carbon emissions as compared to 2005 by 2025; the reduction in carbon emissions by 43% compared to 2005 by 2030 and the increase of the share of biofuels in the Brazilian Energy Matrix to 18% by 2030 (Brazil, 2016). Moreover, with RENOVABIO, the Brazilian Government has recently established an objective of reducing GHG emissions by 10.1% until 2028 (UDOP, 2018). Nevertheless, without a clear overview of the biogas and biomethane potentials, uses and barriers in Brazil, this bioenergy faces difficulty in developing a consumer market.

An important step in estimating the biomethane potential are the cleaning and upgrading processes to transform biogas into biomethane. The cleaning process removes harmful impurities, such as H_2S, NH_3, siloxanes and moisture. The upgrading process removes CO_2, adjusting the calorific value of the fuel and the gas composition to conform to a given biomethane standard (Ryckebosch et al., 2011). Biogas treatment has attracted attention, and many technologies have been developed and applied, especially for H_2S and CO_2 separation. The several combinations of technologies may form different biogas upgrading process configurations, and dominating the fundamentals of these processes, which usually involves complex thermodynamic and transport phenomena principles, or using expansive simulation software might be necessary for assessing biomethane production. These tools are not always readily available to policy makers and energy planners, who might be tempted to admit oversimplified solutions (such as considering no loss of methane in the upgrading process) to assess the production rate of biomethane, its composition and its energy content to reach a given quality standard. A simple, yet accurate methodology for estimating biomethane production after biogas upgrading, as well as for estimating other important parameters of biomethane is of paramount importance to assess potentials with low uncertainty and greater reliability for energy and environmental policy and planning. In places such as São Paulo, which already have a solid regulatory environment for biogas and biomethane, a reliable and concrete potential estimation is the last step to convince stakeholders to invest in the biomethane market.

In view of the aforementioned, we here present a short-cut model to estimate biomethane availability after biogas cleaning and upgrading using only information regarding biogas and biomethane composition. The objective of this model is to present a methodology to policymakers and energy planners to estimate biomethane availability after biogas cleaning and upgrading. This paper is a part of one of the thematic projects of the Research Centre for Gas Innovation (RCGI) of the University of São Paulo. The objective of this thematic project is to identify and to quantify biogas and biomethane potentials, to propose technological routes for biogas and biomethane production and to explore policies for biogas and biomethane incentive in Brazil. Therefore, the model developed is a crucial tool for the referred project.

The work is structured as follows. In section 2, we give a brief outlook of the main biogas cleaning and upgrading technologies to highlight the most important information for the model input. In section 3, we show the methodology for developing the model. In section 4, the results are presented, confronting the model with literature data; in this section, we also present a case study, in which the model is applied to predict the biomethane potential from biogas produced by ethanol vinasse digestion in the state of São Paulo, showing how energy planners and policymakers can use the model to estimate biomethane production and avoided GHG emission by substituting biomethane by fossil fuels. Finally, in section 5, the conclusion of this study are presented.

2. Biogas cleaning and upgrading

Biogas cleaning and upgrading has been vastly studied in the literature. Ryckebosch et al. (2011) reviewed the main techniques for removing water, H_2S and CO_2, focusing on comparing the advantages and disadvantages of technologies for removing each component; Abatzoglou and Boivin (2009) reviewed the state-of-the-art of biogas cleaning techniques focusing on H_2S removal, detailing mechanisms and presenting technical data. Other reports direct attention to the damaging effects of trace compounds and to their removal technologies, such as Rasi et al. (2011) for volatile organic compounds (VOCs) and Ajhar et al. (2010) for siloxanes, usually present in biogas from wastewater treatment plants and landfills, respectively. Most studies, however, evaluate the upgrading process. Many reviews have been published for presenting the available technologies and comparing their performances based on data available in the literature, such as Sun et al. (2015) and Yang (2014). Patterson et al. (2011) also presents a review to support economic scenarios of biogas use in waste collection systems. Leme and Seabra (2017) and Collet et al. (2017) developed their own models and process flow diagrams of the different technologies for technical-economic assessments of biomethane production. Simulations are often used as a tool for evaluating process performances and parameters influence in studies that compare different technologies, such as Molino et al. (2013), Xu et al. (2015), and Morero et al. (2017), or that detail a particular one, such as Wylock and Budzianowski (2017) (which details water scrubbing) Leonzio (2016) (which details chemical absorption) and Yousef et al. (2016) (which presents an alternative process for biogas upgrading). The energy performance of the systems is also often analyzed, as in Sun et al. (2015), which compares the main upgrading technologies, Rotunno et al. (2017), which focuses on water scrubbing and Valenti et al. (2016), which focuses on membrane technology.

Table 1
H_2S removal technologies (adapted from Deublein and Steinhauser, 2008).

H_2S removal technology	Level of decontamination	Air intake into biogas required
Internal biological desulfurization	Very rough	Yes
Percolating filter plant	Rough	Yes
Bioscrubber plant	Rough	No
Sulfide precipitation	Rough	No
Ferric chelate	Rough	Yes
$Fe(OH)_3$ – bog iron ore	Fine	Both options
Fe_2O_3	Fine	Both options
Activated carbon – KI, K_2CO_3, $KMnO_4$	Fine	No
Zinc oxide	Fine	No
Surfactant	Fine	No
Absorption by glycol and ethanolamine	Fine	No
Algae	Fine	Yes
Direct oxidation	Fine	Yes

It is not the objective of this paper to address in detail all of the cleaning and upgrading technologies and the physical chemical processes involved, since the literature on this topic is plentiful. Nevertheless, it is important to give a brief outlook of the main technologies and to highlight the aspects of each one that will have impact on the proposed short-cut model.

Biogas composition greatly depends on the organic feedstock source and on the anaerobic digestion conditions, but it mainly consists of CH_4 and CO_2, with traces of other contaminants, such as H_2S, NH_3 and water vapor. Thus, the separation of gases that are not methane is the focus of the cleaning process (removal of contaminants) and the upgrading process (removal of CO_2 for adjusting the calorific value of the gas).

The removal of H_2S and other contaminants is critical because, despite having lower concentration, they may have corrosive or clustering power when combined. Therefore, the separation of these components from biogas is a relevant stage in the production of biomethane, both in terms of guaranteeing the system performance and the costs involved. Hence, the removal of H_2S, as well as other damaging contaminants, such as water and siloxanes, if present, should occur in an upstream stage in the process (Patterson et al., 2011).

The desulfurization step may be classified by the technique capacity of rough or fine decontamination (Deublein and Steinhauser, 2008). While, in some cases, the requirements may be met using only one decontamination technique, it is common to combine two methods in processes that present high H_2S concentrations and/or require low values of H_2S, such as in biomethane production (Leme and Seabra, 2017). In this case, technologies that require air intake should be avoided, so that biogas is not contaminated with N_2 and O_2, gases that are difficult to remove. Table 1 presents the main technologies for H_2S removal and its characteristics.

Besides H_2S removal, biomethane production may require other cleaning steps. Raw biogas has a saturated content of water vapor, which may condensate, causing corrosion and clogging in pipes, and is considered a contaminant for some upgrading technologies. Thus, dehydration must occur at an early stage. Depending on the feedstock used for biogas production, other contaminants may be present, such as siloxanes, common in sewage treatment stations and landfill gas. Siloxanes form SiO_2 after combustion and microcrystalline quartz deposited on engine or turbines surfaces, causing severe damages (Yang, 2014). Siloxanes, as well as ammonia, halogen compounds, N_2 and O_2 can make the cleaning process even more complex (e.g. requiring a combination of techniques or increased consumption of separation media).

Carbon dioxide removal (i.e. the upgrading process), on the other hand, usually takes only one among the many technologies available that can meet the standards by itself, which allows an easier comparison of their performances. Many studies have reviewed biogas upgrading technologies, analyzing parameters such as energy consumption, methane losses and methane purity achieved in the biomethane (Sun et al., 2015). Table 2 shows the most reported upgrading technologies.

It is often mentioned that the choice of the upgrading technology depends on the conditions and characteristics of the plant. As Sun et al. (2015) describes, the choice "must be site-specific and case sensitive". To minimize the cost per unit of biomethane, one must analyze investment and operational costs, including the affordability and availability of the equipment, raw material, specialized labor, electricity and heat consumption. However, it is important that the process meets the composition requirements and its safety and environmental risks are adequate to the plant site installations (Leme and Seabra, 2017).

3. Methods

3.1. Model

In the proposed model, the upgrading and cleaning system model is a black box, i.e.: the model will only concern the inputs and outputs of the control volume, regardless of the process employed, thermodynamics or transport kinetics. Fig. 1 shows the proposed black box model. Table 3 presents all the variables used on the model. The conditions for volumetric variables are the normal conditions (273.15 K and 101,325 Pa) and the concentrations are on dry base.

Another important aspect of the model is that, even though its variables are mass-based, specifications for biomethane commonly express the gas composition in terms of its volumetric fractions.

Table 2
Biogas upgrading technologies (adapted from Probiogas (2010); Yang (2014); Sun et al. (2015); Leme and Seabra (2017)).

Upgrading technology	CH_4 losses (typical)	CH_4 (%v/v) in biomethane	Energy consumption[a] (kWh/Nm^3_{biom})	Observations
Water scrubbing	Low (1–3%)	>98%	0.45–0.90 (EE)	High water demand; removes NH_3
Physical absorption	Low-Medium (2–4%)	>96%	0.49–0.67 (EE)	Different organic solvents available; removes H_2S, but may hinder the regeneration of the solvent
Chemical absorption (amine scrubbing)	Very low (<0.1%)	>99%	0.12–0.30 (EE) 0.44–1.64 (H)	High heat demand; Low electricity consumption; removes H_2S; may produce high quality CO_2
Pressure swing adsorption (PSA)	Medium-High (4–9%)	>97%	0.30–1.00 (EE)	N_2/O_2 removal possible; requires fine H_2S pre-removal to protect adsorbent material
Membrane separation	Low-High (1–12%)	>96%	0.25–0.43 (EE)	Compact; low-medium energy requirements; membrane can be expensive
Cryogenic Separation	Very low (0.5–1%)	>97%	0.80–1.45 (EE)	New technology; High energy consumption; Possible removal of O_2 and N_2

[a] EE = Electric Energy; H= Heat.

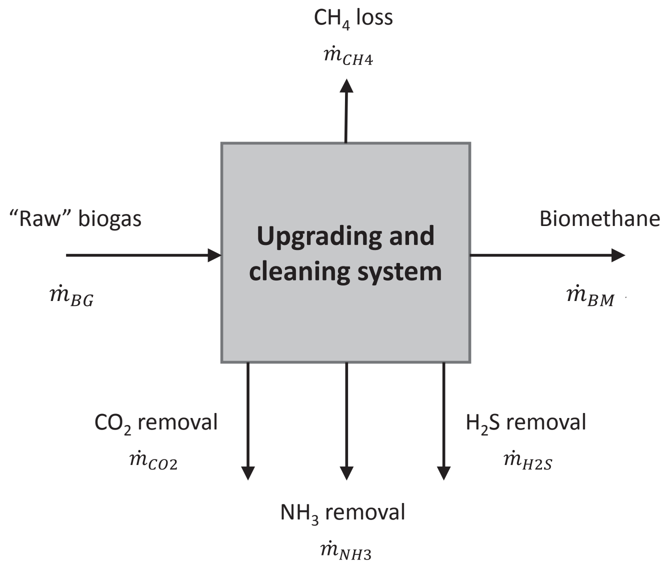

Fig. 1. Black-box model for biogas cleaning and upgrading.

Thus, a conversion from mass fraction to volumetric fraction is necessary. Equation (1) expresses the conversion of volumetric fraction into mass fraction:

$$x_i = \frac{\rho_i \cdot y_i}{\rho_T} \tag{1}$$

In equation (1) x_i is the mass fraction, y_i is the volumetric fraction, ρ_i is the density of a component *i* and ρ_T is the total density of the gas mixture.

The model uses some simplifying assumptions, listed below:

- Inert gases (N_2 and O_2) are not captured by the cleaning and upgrading system;
- A loss stream exists, but it is composed solely of methane;
- Biogas enters the cleaning and upgrading systems at a dry state;
- The thermodynamic behavior of the gas is assumed to be ideal, following the ideal gas model;
- The thermodynamic behavior of the gas mixture is assumed to be ideal.

Table 3 shows expressions using both mass and volumetric fractions. Even though analytic methods and standards usually present results using volumetric factions, the model requires mass fractions for the mass balance. Browsing through the expressions presented, it becomes clear that, to determine the value of the mass fraction of a component, the total density of the gas mixture, which also depends on the mass fraction of this component, must be also determined. Hence, the problem becomes iterative and rather difficult to solve. It might be more practical to simply calculate $x_i = \frac{\rho_i \cdot y_i}{\sum \rho_i \cdot y_i}$ to first determine the mass fraction of each component and later calculate the total mixture density. Estimation for the individual density of each component comes from the ideal gas model behavior. Should the biogas or biomethane density be easily accessible data (found in the literature or a project data), the first expression yields faster results.

The global and component mass balance yields the following equations:

$$\text{Global mass balance}: \dot{m}_{BG} = \dot{m}_{CH4} + \dot{m}_{CO2} + \dot{m}_{H2S} + \dot{m}_{NH3} + \dot{m}_{BM} \tag{2}$$

$$CH_4 \text{mass balance}: x'_m \cdot \dot{m}_{BM} + \dot{m}_{CH4} = x_m \cdot \dot{m}_{BG} \tag{3}$$

$$CO_2 \text{ balance}: \dot{m}_{CO2} = x_c \cdot \dot{m}_{BG} - x'_c \cdot \dot{m}_{BM} \tag{4}$$

$$H_2S \text{ balance}: \dot{m}_{H2S} = x_s \cdot \dot{m}_{BG} - x'_s \cdot \dot{m}_{BM} \tag{5}$$

$$NH_3 \text{ balance}: \dot{m}_{NH3} = x_n \cdot \dot{m}_{BG} - x'_n \cdot \dot{m}_{BM} \tag{6}$$

$$\text{Inert balance}: (1 - x'_m - x'_c - x'_s - x'_n) \cdot \dot{m}_{BM} = (1 - x_m - x_c - x_s - x_n) \cdot \dot{m}_{BG} \tag{7}$$

In order to use a recurring performance parameter of methane-concentrating technologies, the rate of methane loss will be accounted as a factor of loss related to the input rate of methane

Table 3
Model variables.

Variable		Biogas	Biomethane
Flowrate	Mass (kg/s)	$\dot{m}_{BG}$	$\dot{m}_{BM}$
	Volumetric (Nm^3/s)	$Q_{BG} = \frac{\dot{m}_{BG}}{\rho_{BG}}$	$Q_{BM} = \frac{\dot{m}_{BM}}{\rho_{BM}}$
Density	kg/Nm^3	$\frac{1}{\rho_{BG}} = \sum \frac{x_i}{\rho_i}$ or $\rho_{BG} = \sum y_i \cdot \rho_i$	$\frac{1}{\rho_{BM}} = \sum \frac{x'_i}{\rho_i}$ or $\rho_{BM} = \sum y'_i \cdot \rho_i$
Composition (volumetric fraction)	CH_4 (% vol)	y_m	y'_m
	CO_2 (% vol)	y_c	y'_c
	H_2S (% vol)	y_s	y'_s
	NH_3 (% vol)	y_n	y'_n
	Inert (% vol)	$y_{in} = 1 - y_m - y_c - y_s - y_n$	$y'_{in} = 1 - y'_m - y'_c - y'_s - y'_n$
Composition (mass fraction)	CH_4 (% wt)	$x_m = \frac{\rho_m \cdot y_m}{\rho_{BG}}$ or $\frac{\rho_m \cdot y_m}{\sum \rho_i \cdot y_i}$	$\frac{\rho_m \cdot y_m}{\rho_{BM}}$ or $\frac{\rho_m \cdot y'_m}{\sum \rho_i \cdot y'_i}$
	CO_2 (% wt)	$x_c = \frac{\rho_c \cdot y_c}{\rho_{BG}}$ or $\frac{\rho_c \cdot y_c}{\sum \rho_i \cdot y_i}$	$x'_c = \frac{\rho_c \cdot y'_c}{\rho_{BM}}$ or $\frac{\rho_c \cdot y'_c}{\sum \rho_i \cdot y_{ni}}$
	H_2S (% wt)	$x_s = \frac{\rho_s \cdot y_s}{\rho_{BG}}$ or $\frac{\rho_s \cdot y_s}{\sum \rho_i \cdot y_i}$	$x'_s = \frac{\rho_s \cdot y'_s}{\rho_{BM}}$ or $\frac{\rho_s \cdot y'_s}{\sum \rho_i \cdot y'_i}$
	NH_3 (% wt)	$x_n = \frac{\rho_n \cdot y_n}{\rho_{BG}}$ or $\frac{\rho_n \cdot y_n}{\sum \rho_i \cdot y_i}$	$x'_n = \frac{\rho_n \cdot y_m}{\rho_{BM}}$ or $\frac{\rho_n \cdot y'_n}{\sum \rho_i \cdot y'_i}$
	Inert (% wt)	$x_{in} = 1 - x_m - x_c - x_s - x_n$	$x'_{in} = 1 - x'_m - x'_c - x'_s - x'_n$

(f_{loss}):

$$\dot{m}_{CH4} = x_m \cdot \dot{m}_{biog} \cdot f_{loss} \tag{8}$$

The proposed model will derive from the combination and rearrangement of equations (2)–(8) and the introduction of the following dimensionless parameters:

$$X_{BM/BG} = \frac{\dot{m}_{BM}}{\dot{m}_{BG}} \text{ – mass conversion factor of biogas into biomethane by the process;} \tag{9}$$

$$Y_{BM/BG} = \frac{Q_{BM}}{Q_{BG}} \text{ – volumetric conversion factor of biogas into biomethane by the process;} \tag{10}$$

$$r = \frac{1}{1 - x_c - x_s - x_n} \text{ – biogas mass contamination factor;} \tag{11}$$

$$r' = \frac{1}{1 - x'_c - x'_s - x'_n} \text{ – biomethane mass contamination factor;} \tag{12}$$

$$r_m = \frac{1}{x_m \cdot f_{loss}} \text{ – methane mass retention factor of the upgrading and cleaning system} \tag{13}$$

$$R_i = \frac{\dot{m}_i}{x_i \cdot \dot{m}_{BG}} \text{ – mass removal factor of the contaminant } i \text{ in the upgrading and/or cleaning system} \tag{14}$$

The objective is to present a model that consists only of dimensionless parameters to predict the biomethane availability after any given biogas cleaning and upgrading process. Once this model is proposed, other important parameters, such as the biomethane lower/higher heating value (LHV/HHV)will be combined to it. In order to validate the model, this study searched for data from case studies, experiments or simulation of biogas upgrading, such as composition and flowrates, and the parameters $X_{BM/BG}$, r and r' were calculated and fitted to the model using the software Microsoft Excel®. This study uses graphic correlations to assess the fitting of the data to the model.

4. Results

4.1. Model development

By manipulating equations (2)–(8) and using the dimensionless parameters (9)–(14), equation (15) is obtained. This equation correlates the conversion factor with the gas quality factors before and after the upgrading and cleaning process and with the methane retention by the process. Equation (16) shows the methane concentration, obtained by combing equations (3), (5) and (15).

$$X_{BM/BG} = r' \cdot \left(\frac{1}{r} - \frac{1}{r_m} \right) \tag{15}$$

$$x'_m = \frac{x_m - 1/r_m}{X_{BM/BG}} \tag{16}$$

Although it may vary greatly according to the organic matter feedstock, biogas composition typically remains within a quite narrow range of values. Table 4 shows these typical values, as well as the typical biomethane concentration and the parameter r or r' for each case.

In order to determine the value of the CO_2 concentration in biomethane, the dimensionless parameter R_{CO2} is necessary. Combining equations (4) and (14), one obtains:

$$x'_c = x_c \cdot \frac{1 - R_{CO2}}{X_{BM/BG}} \tag{17}$$

Similarly, the H_2S concentration after the upgrading process will be given by equation (18):

$$x'_s = x_s \cdot \frac{1 - R_{H2S}}{X_{BM/BG}} \tag{18}$$

Finally, in order to obtain the volumetric conversion of biogas into biomethane ($Y_{BM/BG}$), simply manipulating equations (9) and (10) yields equation (19):

$$Y_{BM/BG} = X_{BM/BG} \cdot \frac{\rho_{BG}}{\rho_{BM}} \tag{19}$$

Table 4
Typical dry biogas composition according to organic matter feedstock and typical dry biomethane composition (adapted from Allegue and Hinge, 2012; Ett et al., 2013).

Parameter	Wastewater treatment plants		Household waste		Agricultural wastes		Biomethane	
Classification	Poor	Rich	Poor	Rich	Poor	Rich	Poor	Rich
CH_4 (%wt)	37.70	58.30	30.00	39.10	35.80	57.00	90.00	97.00
CO_2 (%wt)	57.00	40.60	62.70	60.90	54.10	39.70	4.90	3.00
N_2+O_2 (%wt)	1.70	0.00	6.50	0.00	1.60	0.00	3.06	0.00
H_2S (%wt)	3.50	1.10	0.80	0.10	8.40	3.20	0.02	0.00
NH_3 (%wt)	0.00	0.00	0.00	0.00	0.10	0.10	0.02	0.00
r or r'	2.646	1.715	3.333	2.564	2.793	1.754	1.183	1.153

where $\rho_{BG/m}$ and $\rho_{BM/m}$ are the specific gravities of biogas and biomethane, respectively, which are easily calculated using the equations in Table 3.

Another important parameter for biomethane, usually required by standards, is its energy content (measured by the HHV or LHV). The biomethane energy content is the weighted average of each of its components energy content. Since the concentrations of H_2S and NH_3 are usually very low on biomethane, the model disregards these components contributions. Additionally, being inert to combustion, CO_2 does not contribute to the LHV, either. Thus, only the methane contribution will take place, leading to equation (20).

$$LHV_{BM} = LHV_m \cdot \frac{x_m - 1/r_m}{X_{BM/BG}} \quad (20)$$

Note that equation (19) can also be expressed in terms of methane HHV and/or in volumetric terms.

4.2. Model validation

Table 5 shows the data retrieved from the literature already in the form of the calculated parameters of the model. When plotting $X_{BM/BG}$ against $r' \cdot (1/r - 1/r_m)$, a linear correlation with angular coefficient equal to 1 and linear coefficient equal to zero is expected. Fig. 2 shows the data plotted against the model.

Fig. 2 allows perceiving that the model fits quite well to data from the literature, even when the methane loss is high. The fitting to the model is very satisfactory, with a fitting parameter R^2 of 0.985.

Fig. 3 shows the calculated LHV using the model. A threshold of the minimum and maximum LHV calculated from Table 2 with 5% tolerance was chosen as the range of acceptable values. Most of the results fall within the established range, with few exceptions.

4.3. Case study

According to Joppert et al. (2018), the greatest potential for biogas and biomethane in São Paulo, which concentrates almost 50% of the ethanol production in Brazil (UNICA, 2018), derives from vinasse. Vinasse is a wastewater produced as a by-product of ethanol production. It has high organic load, low pH and high mineral content, and its current use is the fertigation of the sugarcane harvest (Christofoletti et al., 2013). There are many environmental concerns regarding the disposal of vinasse on the soil (Oliveira et al., 2013), and the literature points out that an alternative route for the valuation of vinasse is promoting its biodigestion. This process produces biogas and an effluent that maintains the mineral content of vinasse, but presents reduced organic load (Bernal et al., 2017) - thus, this effluent can still be used for fertigation, with the advantage of reduced environmental impacts (Nogueira et al., 2015).

Although sugarcane ethanol is a biofuel, ethanol production produce important GHG emissions, mainly from diesel oil (DO) burning in heavy-duty machinery for harvesting and trucks for transporting sugarcane (Macedo et al., 2008). There are two forms in which biomethane may aid in reducing the GHG emissions in ethanol plants: directly, by adapting the engines of the machinery and trucks to run on biomethane, thus displacing DO and indirectly, by injecting biomethane on NG pipelines, increasing the energy supply without increasing. Thus, biomethane will play an important role in enabling ethanol plants to help to reduce GHG emissions and meet the goals established by the Paris Agreement.

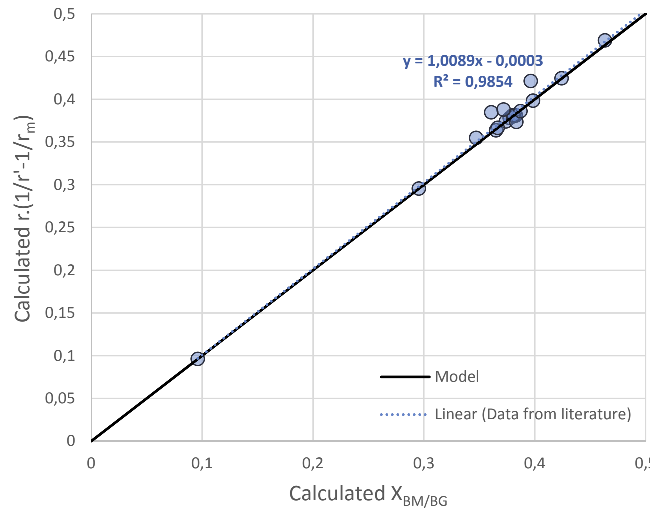

Fig. 2. Data and model correlation.

Table 5
Data from literature.

Data	Upgrading technology	Methane loss	Calculated $X_{BM/BG}$	Calculated $r.(1/r'-1/r_m)$	Reference
1	Water scrubbing	2.0%	0.378	0.378	Leme and Seabra, 2017
2	Organic scrubbing	3.0%	0.374	0.374	Leme and Seabra, 2017
3	Amine scrubbing	0.5%	0.365	0.363	Leme and Seabra, 2017
4	Membrane	1.0%	0.367	0.367	Leme and Seabra, 2017
5	PSA	8.0%	0.347	0.355	Leme and Seabra, 2017
6	Water scrubbing	0.5%	0.381	0.381	Rotunno et al., 2017
7	Water scrubbing	0.5%	0.381	0.381	Rotunno et al., 2017
8	Water scrubbing	0.5%	0.382	0.381	Rotunno et al., 2017
9	Water scrubbing	0.5%	0.380	0.381	Rotunno et al., 2017
10	Water scrubbing	0.5%	0.383	0.381	Rotunno et al., 2017
11	Water scrubbing	0.5%	0.381	0.381	Rotunno et al., 2017
12	Caustic scrubbing	1.0%	0.096	0.096	Leonzio, 2016
13	Membrane	11.5%	0.295	0.295	Valenti et al., 2016
14	Cryogenic separation	0.2%	0.399	0.398	Yousef et al., 2016
15	Water scrubbing	Neg.	0.383	0.373	Xu et al., 2015
16	Water scrubbing	3.5%	0.387	0.386	Morero et al., 2017
17	Amine scrubbing	Neg.	0.397	0.421	Collet et al., 2017
18	Membrane	7.5%	0.372	0.388	Collet et al., 2017
19	Water scrubbing	1.0%	0.424	0.424	Wylock and Budzianowski, 2017
20	Membrane	14.8%	0.463	0.469	Molino et al., 2013
21	N/A	1.0%	0.361	0.385	NREL, 2012

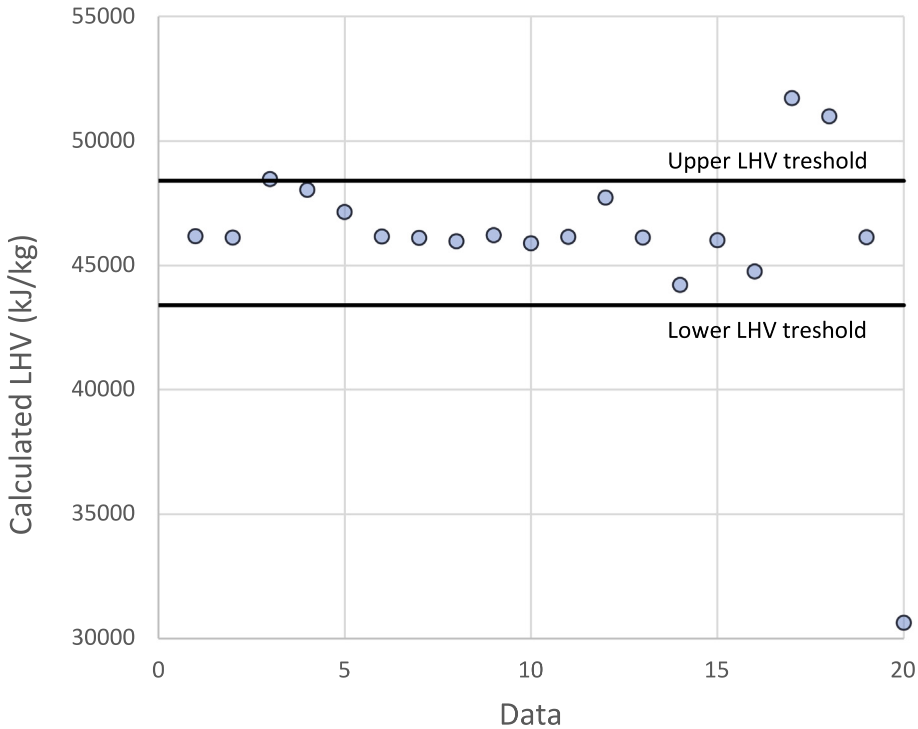

Fig. 3. Model fitting for LHV.

Given these facts, a case study focusing on predicting the biomethane potential for this state is presented in this section. This case study uses the proposed model to predict the biomethane availability after cleaning and upgrading of biogas produced from vinasse. In the context of the goals to reduce GHG emissions, the avoided GHG emissions caused by using biomethane to displace DO or NG are also calculated.

4.3.1. Biogas production and DO consumption

To estimate the potential of biogas in the State of São Paulo, be it for biomethane injection or biomethane burning in gas engines, the first step is to assess the production of ethanol in the region in a given period of time. Then, using typical values of the ratio of vinasse production to the ethanol production and the ratio of biogas to vinasse digested, as well as adopting a typical composition for biogas, one can estimate the theoretical amount of biogas produced in the state of São Paulo. Finally, using the model proposed herein, the biomethane to biogas ratio in the upgrading process can be derived to meet the standards of biomethane in Brazil. Thus, the biomethane potential for the State of São Paulo is estimated using equation (21):

Table 6
Biomethane specification as regulated by ANP resolution 685/2017 for the state of São Paulo.

Parameter[a]		Limits
CH_4 (min)	% mol	90.0
O_2 (max)	% mol	0.8
CO_2 (max)	% mol	3.0
CO_2+O_2+N_2 (max)	% mol	10.0
S, total (max)	mg/m^3	70.0
H_2S (max)	mg/m^3	10.0
HHV	MJ/Nm^3	35–43

[a] Values for dry biogas at 293.15 K and 101.325 kPa.

$$Q_{BM} = Q_{EtOH}\cdot\frac{Q_{vin}}{Q_{EtOH}}\cdot\frac{Q_{BG}}{Q_{vin}}\cdot\frac{Q_{BM}}{Q_{BG}} \quad (21)$$

where Q_{EtOH} (m$^3{}_{ethanol}$/year) is the annual production of ethanol in a given sugarcane harvest, $\frac{Q_{vin}}{Q_{EtOH}}$ (m$^3{}_{vinasse}$/m$^3{}_{ethanol}$) is the vinasse to ethanol production ratio, $\frac{Q_{BG}}{Q_{vin}}$ (m$^3{}_{biogas}$/m$^3{}_{vinasse}$) is the biogas to vinasse production ratio in the biodigestion process and $\frac{Q_{BM}}{Q_{BG}}$ (m$^3{}_{biomethane}$/m$^3{}_{biogas}$) is the biomethane to biogas ratio in the biogas upgrading process, which will be derived from the model developed herein.

The above-mentioned ratios and the biogas composition were obtained from Joppert et al. (2017), who used these parameters to study the use of biogas produced from vinasse in UASB reactors to displace sugarcane bagasse towards 2G ethanol production. Thus, it is assumed that $\frac{Q_{vin}}{Q_{EtOH}} = 13.0$; $\frac{Q_{biog}}{Q_{vin}} = 21.54$. The assumed biogas from vinasse biodigestion volumetric composition is 65% CH_4, 33.2% CO_2, 0.3% H_2S, 1.5% inert and it is also assumed that $R_{H2S} = 0.999$, derived from the same study.

To estimate DO consumption in the mill, we consider a specific consumption of 400L/ha of DO (Macedo et al., 2008) and an ethanol productivity of 6417 L/ha (Goldemberg, 2009), resulting in a specific consumption of 0.062 L_{DO}/L_{EtOH}

4.3.2. Biomethane standard

In Brazil, the biomethane standard is in a process of improvement. Currently, the National Agency for Oil, Natural Gas and Biofuels (ANP) regulates the biomethane composition and energy content through resolution 685/2017 (this resolution incorporates and modifies ANP resolution 08/2015, which was the prior biomethane standard in Brazil) (ANP, 2017). ARSESP deliberation 744 states that, in São Paulo, biomethane may only be used as vehicular fuel or injected in the gas pipeline if it complies with this resolution

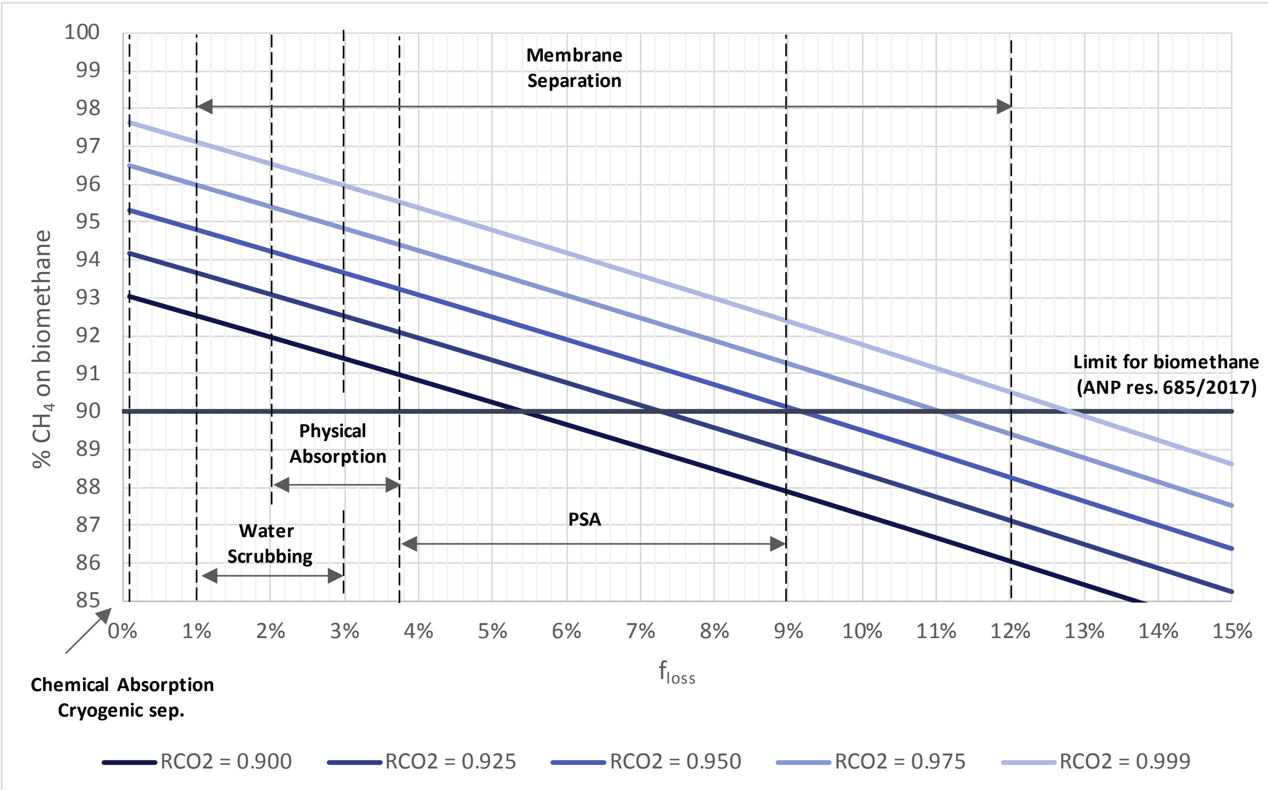

Fig. 4. Sensitivity analysis for methane concentration in biomethane after cleaning and upgrading ($R_{H2S} = 0.999$).

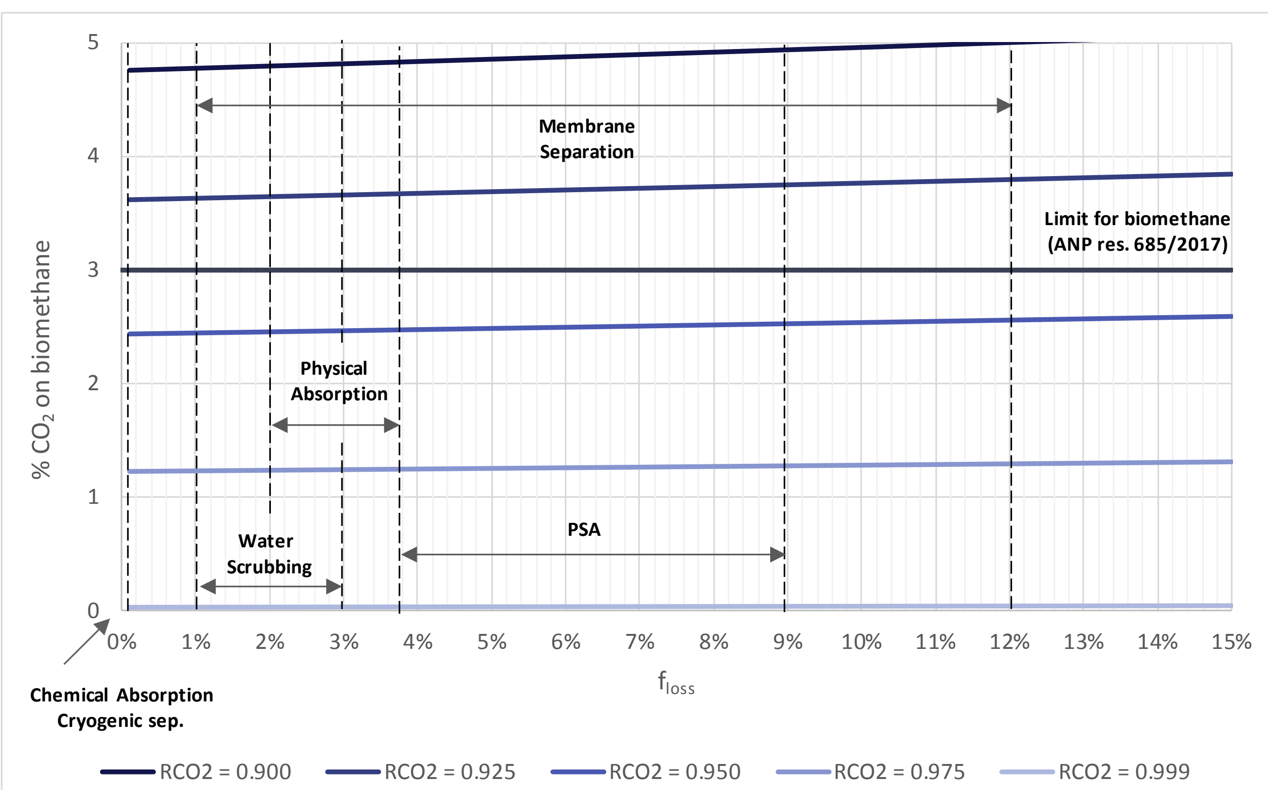

Fig. 5. Sensitivity analysis for CO_2 concentration in biomethane after cleaning and upgrading ($R_{H2S} = 0.999$).

(ARSESP, 2017). For the region of the state of São Paulo, the biomethane composition should be the one described in Table 6.

4.3.3. Biogas upgrading

We can use the model to estimate the resulting methane content after biogas cleaning and upgrading and make a preliminary choice of the upgrading technology based on the results and ANP standard for biomethane. As stated in section 4.1, x'_m is a function of x_m, $X_{BM/BG}$ and f_{loss}, while $X_{BM/BG}$ is a function of x_c, x_s, R_{CO2} and R_{H2S}. x_m, x_c and x_s are given, since the biogas composition is known. Thus, the only open parameters are R_{CO2}, R_{H2S} and f_{loss}. It is thus possible to plot x'_m through a sensitivity analysis varying R_{CO2} and f_{loss}. The results are shown in Figs. 4–6.

Figs. 4–6 also show the typical range of f_{loss} for the main upgrading technologies and the methane concentration, CO_2 concentration and HHV limits given for injecting biomethane in the NG grid. Fig. 4 shows that, for achieving the ANP standard for methane concentration, R_{CO2} can be as low as 0.9, but the maximum f_{loss} must be between 5% and 6%. However, looking at Fig. 5, it becomes clear that R_{CO2} must be higher than 0.9 to achieve the standard for CO_2 concentration (it must be above 0.94), and that f_{loss} has little effect on the CO_2 concentration. As for Fig. 6, results similar to those observed in Fig. 4 can be implied, which is logical, since the main contribution for biomethane HHV is the methane concentration. Thus, the limiting factor for the upgrading process is to set the CO_2 concentration to 3%, which is achieved if $R_{CO2} \approx 0.94$.

Fig. 4 demonstrates that methane medium methane losses are available to achieve both methane concentration and HHV criteria, but high methane losses are prohibitive. It is hence possible to conclude that the membrane separation technology is not the best choice for upgrading the biogas in this case study. However, it is not necessary to use technologies with low methane losses, such as cryogenic separation, chemical absorption and water scrubbing. These technologies have high energy consumption and high operation and maintenance costs (Sun et al., 2015) and would not be an economic choice. The best upgrading technology seems to be PSA, which has moderate energy consumption, operation and maintenance costs (Sun et al., 2015).

The upgrading process will consume electric power. Ethanol and sugar mills produce their own energy through bagasse burning to meet the plant energy needs and generate a surplus, which is sold to the electric grid (Joppert et al., 2017). Thus, the plants might not be willing to consume more electric energy, which would reduce the amount of energy they sell. Therefore, in the case study, we assume that a part of the biogas produced will be burned on a gas engine to generate the amount of energy necessary for biogas upgrading. The amount of biogas consumed is given by equation (22):

$$Q_{BG,c} = Q_{BG} \cdot \left(\frac{Y_{BM/BG} \cdot w_{up}}{Y_{BM/BG} \cdot w_{up} + y_m \cdot LHV_m \cdot \eta_T \cdot f_c} \right) \quad (22)$$

where $Q_{BG,c}$ (Nm^3/y) is the consumed biogas for the energetic demand of the upgrading process, Q_{BG} (Nm^3/y) is the total biogas production assessed on item 4.3.1, w_{up} (kWh/Nm^3) is the specific power consumption of the given upgrading process, which, for PSA, we assume an average value of 0.65 (Sun et al., 2015), η_T is the thermic efficiency of the gas engine, which is 33% (Bernal et al., 2017), and f_c is the load factor for the gas engine, which we assume to be 0.8.

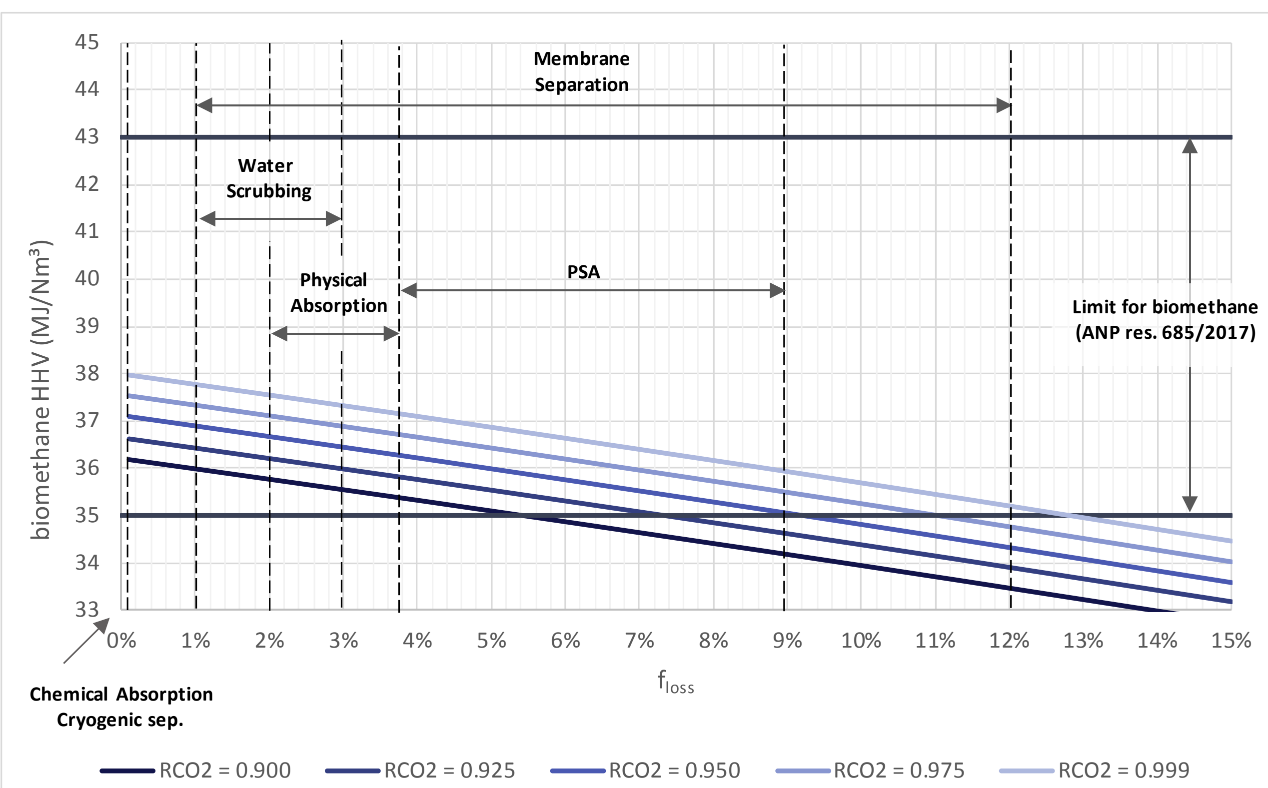

Fig. 6. Sensitivity analysis for biomethane HHV after cleaning and upgrading ($R_{H2S} = 0.999$).

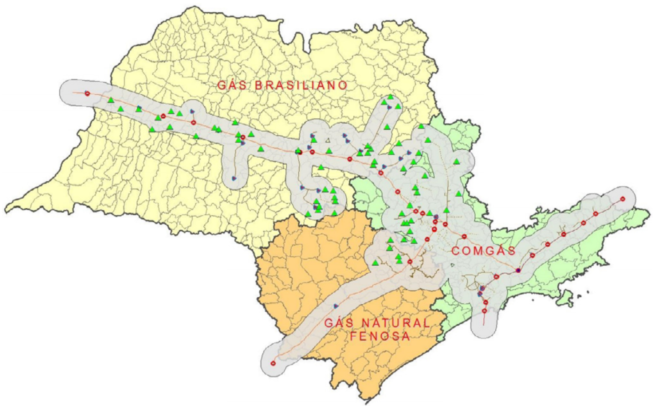

Fig. 7. Ethanol plants in the state of São Paulo within a 20 km range from the existing NG pipelines (EPE, 2017a).

4.3.4. GHG emissions avoided

Regarding the substitution of fossil fuels, the substitution of NG is direct (through the injection of biomethane in the gas grid), but it is not direct with DO: adaptations are required to transform the Diesel cycle engine into an Otto cycle engine (Avellar and Luczynski, 2012) and there are limiting requirements regarding CH_4 and CO_2 content in biomethane for its use in internal combustion engines (Makaruk et al., 2010).

The amount of a given fossil fuel that can be replaced by biomethane is described by equations (23)–(25):

$$Q_{BM,a} = (Q_{BM} - Q_{BM,c}) \cdot Y_{BM/BG} \tag{23}$$

$$Q_F = \frac{(1-\eta_{loss}) \cdot Q_{BM,a} \cdot LHV_{BM}}{LHV_F} \tag{24}$$

$$E_{GHG} = Q_F \cdot LHV_F \cdot e_F \tag{25}$$

where Q_F (Nm^3/y or L/y) is the amount of fossil fuel displaced, $Q_{BM,a}$ is the available biomethane production (Nm^3/y), η_{loss} is the efficiency loss in the case of converting a Diesel engine to and Otto engine causes an efficiency loss, which is reported to be 13% (Camuzeaux et al., 2015) (η_{loss} is zero in the case of NG substitution), LHV_F is the LHV of the fossil fuel (36.6 MJ/Nm^3 for NG and 36.3 MJ/l for DO (IPCC, 2006)) and e_F is the specific GHG emission for the fossil fuel (56.1 kg/GJ for NG and 74.1 kg/GJ for DO (IPCC, 2006)).

4.3.5. Biomethane potential from vinasse and GHG mitigation

Using the proposed model, the biomethane production is assessed, as well as the amount of fossil fuel (DO and NG) replaced and the amount of GHG emissions avoided. In both cases, the select upgrading technology will be PSA.

To decide which ethanol and sugar mills will be able to inject biomethane on the gas grid, we assume a study developed by the Secretariat of Mining and Energy of the State of São Paulo, which selected mills that were at a maximum distance of 20 km from the existing NG infrastructure in the State of São Paulo as the ones that would present economic feasibility to inject biomethane in the NG grid (EPE, 2017a,b). The study identified that 66 out of the 197 ethanol plants of the state are within this range, which can be seen in Fig. 7. The ethanol production data was retrieved for each mill (Pró Cana, 2016; DATAGRO, 2017). This case study assumes that the amount of biogas from vinasse produced by these 66 mills, after cleaning and upgrading, are to be injected in the NG pipelines, complying with ANP resolution 685/2017. This case study also assumes that the remainder of the biogas from vinasse production in the state, after cleaning and upgrading, will be used to displace DO from the heavy-duty machinery and trucks, and will also be complying with ANP resolution 685/2017.

Table 7 shows the model inputs. The data for ethanol production corresponds to the 2016/2017 harvest. The total production of ethanol was retrieved from UNICA (2018). The total biogas potential obtained for the State of São Paulo is 3.735×10^9 Nm^3/y. Joppert et al. (2018) estimated a production of 2.61×10^9 Nm^3/y by performing a Monte Carlo simulation with the parameters of biodigestion process. However, the authors pointed out that this figure is significantly lower than vinasse biogas potentials reported by other studies. Santos et al. (2018) estimated that the production of biogas from vinasse of Brazil would be 1.142×10^9 Nm^3/y, but the authors considered only the production of annexed distilleries and assumed different biodigestion yields from the ones adopted in this case study; UNICA (2017) studied scenarios for biodigestion technology and concluded that the biogas potential for Brazil from the 2016/2017 harvest would range between 3.10 and 4.53×10^9 Nm^3/y. The value obtained in this study is higher than those observed in the literature, which may point that the parameters herein adopted were more optimistic than the parameters used in other studies. It can be observed that different studies use different methodologies to asses the vinasse biogas potentials, yielding different results, which may hinder the ability of policymakers and energy planners to evaluate biogas potentials.

Table 8 shows the results for each case regarding total biomethane production and its energy content. The result obtained is in compliance with ANP resolution 685/2017 in terms of composition on energy content. The model estimated that the reduction of biogas volume due to the cleaning and upgrading model is 33%. This result is coherent with the one reported by the Brazilian Ministry of Energy, in which a "process yield" of the purification process is reported to be around 70% (EPE, 2014).

The total fossil fuel substitution and total GHG emissions avoided are presented in Table 9. It can be observed that nearly 20% of

Table 7
Model inputs.

Parameter	NG substitution (biomethane injection in the NG pipeline)	DO substitution (biomethane burning in gas engines)
Mills selection criteria	Distance from existing NG pipelines $\leq$ 20 km	Distance from existing NG pipelines > 20 km
Mills selected	66	131
Corresponding ethanol production (10^6 m^3/y)	5.568	7.629
Corresponding vinasse production (10^6 m^3/y)	72.387	99.173
Corresponding biogas production (10^9 Nm^3/y)	1.599	2.136
Selected biogas cleaning technology	Iron matrix adsorption	
Selected biogas upgrading technology	PSA	
R_{CO2}	0.940	
R_{H2S}	0.999	
f_{loss}	0.05	

Table 8
Model results.

Biomethane composition	CH_4: 92.0% v/v CO_2: 3.0% v/v Inert: 5.0% v/v H_2S: 4.5 ppm
$Y_{BM/BG}$	0.671
LHV biomethane (MJ/Nm^3)	32.94

the produced biogas must be consumed to generate power for the upgrading process in the case of using PSA. The choice of another upgrading technology with lower methane losses would yield higher CH_4 concentrations on biomethane, but would also cost more biogas consumption to power the upgrading process (for instance, if cryogenic separation was chosen, more than 36% of the produced biogas would have to be consumed). In order to assess the feasibility of the choice of the upgrading technology, this information must be taken into account.

According to the São Paulo State Energy Balance for 2016, the NG consumption was 5.03 10^9 Nm^3 The figure obtained from Table 9 for NG substitution represents 16.6% of the NG consumption of the State of São Paulo in terms of volume and 12.9% in terms of energy content (São Paulo, 2016). These are relevant shares, especially considering that NG comes to São Paulo from Bolivia, through the GASBOL pipeline. Thus, biomethane would raise the energy supply security in São Paulo, by making it less dependent of foreign NG.

Regarding DO, it can be estimated that the ethanol production shown in Table 7 required the consumption of 822.6×10^6 L of fossil fuel. Thus, the DO substitution would not only be able to substitute the fuel in the selected ethanol plants, but also in the other 66 selected for NG injection in the NG pipeline. These figures shows that ethanol plants might be fully independent of DO if they start to use biomethane to power trucks and heavy-duty machinery. This would raise the supply security of ethanol, since the production of biofuel would not stop in case of DO shortage (as happened in May/2018, during the truck drivers strike in Brazil (Nova Cana, 2018)).

The total reduction of GHG emissions would be 3.965×10^6 t_{CO2eq}, which represents 5.48% of the GHG emissions in the State of São Paulo in 2016 (São Paulo, 2016). Considering an emission factor for ethanol plants of 436 t_{CO2eq}/m^3_{EtOH} (Macedo et al., 2008), the total avoided emissions accounts for 68.9% of the emissions of the total number of ethanol plants considered in this study. These figures show the important contribution of biomethane in ethanol plants to achieve the objectives of RENOVABIO and the Paris Agreement.

Even though the figures presented are encouraging, it is worth highlighting that vinasse biodigestion is not currently a reality in Brazil, as it faces a few setbacks, such as:

- The biological process of vinasse biodigestion practically does not reduce the volume of vinasse produced (Poveda, 2014).
- The high amounts of vinasse generated demand high bioreactor capacity (even suing UASB reactors, whose hydraulic retention times are relatively low), causing high investment costs (Gamboa et al., 2012);
- Currently, the thermoresistant antibiotics used in cane juice fermentation hinder the action of the anaerobic bacteria used for vinasse biodigestion. (Moraes et al., 2015).

5. Conclusions

Predicting biomethane availability after biogas cleaning and upgrading might be a challenging task for policymakers and energy planners who do not fully dominate the technical aspects of these processes. Thus, this paper presented a short-cut model to establish a methodology for predicting biomethane availability after biogas cleaning and upgrading. The presented short-cut model allows calculating important parameters of a biogas upgrading process, such as the conversion of biogas into biomethane as well as its LHV. Data from the literature fitted to the model with a R^2 parameter of 0.985, and calculated LHV was within the defined range of acceptable values, which shows a very satisfactory correlation, even for upgrading technologies with high methane losses. Thus, this model offers accurate results, with low uncertainty.

Note that the model, based solely on a mass balance, makes no differentiation between data regarding the organic feedstock for biogas or the technology used to perform the upgrading. Thus, no thermodynamic or kinetic information is necessary, nor is it necessary to use expansive simulation software: only the biogas composition (which can be measured) and the biomethane quality standard (that must be complied with) are necessary. The simplicity of the model makes it very suitable for conceptual engineering projects, policy makers, energy planners and estimation of CO_2 emission reduction, and may provide strategic advantage, especially in countries such as Brazil, where the interest in biomethane environmental and market potentials are increasing.

Using the proposed model in a case study, the paper shows how policymakers and energy planners can use the model for a preliminary choice of the upgrading technology by studying the effects of the model inputs (R_{CO2}, R_{H2S} and f_{loss}) on the biomethane CH_4 content, CO_2 content and energy content and whether it would comply with standards for biomethane. The model results allowed us to assess the consumption of biogas to power the upgrading process, the theoretical potential of biomethane from vinasse and potentials GHG emission reduction for the State of São Paulo by NG replacement by injecting biomethane in the NG pipelines and replacing DO by transforming trucks and heavy-duty machinery engines from Diesel cycle to Otto cycle. The total biomethane produced could replace 16.6% of the State of São Paulo NG consumption in 2016 and replace all the DO used in all the ethanol mills in the state. A total GHG emissions avoidance of 3.965.10^6 t_{CO2eq} could be attained, which represents 5.48% of the GHG emissions of São Paulo in 2016, showing the potential aid of the ethanol plants in the state to achieve the goals established in the Paris Agreement and the Brazilian Government.

Although the model was used for estimating biomethane produced from ethanol vinasse, it can also be used for estimating biomethane production from any other source, such as landfills,

Table 9
Energy consumption in the upgrading process and GHG emissions avoided in the case study.

Parameter	NG substitution (biomethane injection on NG pipeline)	DO substitution (biomethane burning on gas engines)
Consumed biogas (10^9 Nm^3/y)	397.64	544.79
Available biomethane (10^9 m^3/y)	0.833	1.142
Total fossil fuel (NG or DO) displaced	750.0×10^6 Nm^3	901.4×10^6 L
Total GHG emissions avoided (10^6 t_{CO2eq}/y)	1.540	2.425

sewage treatment stations, animal residues, etc. and aid engineers, policymakers and energy planners in assessing biomethane potentials with low uncertainty. The model can also be expanded to take into account other relevant contaminants, such as siloxanes and VOCs, depending on the biomass source for biogas. Lastly, the proposed model should help to guide the evolution of the biomethane standard in Brazil, aiding in establishing the minimum requirements in terms of composition, LHV and other aspects like Wobbe Index in accordance with the existing technologies for biogas upgrading. Further studies should use the proposed model to assess the potentials from other sources of biogas and determine the total biomethane potential of the State of São Paulo and of Brazil as a whole.

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