# **Progress in Energy and Environment**

Journal homepage: https://www.akademiabaru.com/submit/index.php/progee

Link to this article: https://doi.org/10.37934/progee.22.1.2939



Volume 22 (2022) 29-39

Original Article

## Life cycle assessment of Potassium Lysinate for biogas upgrading

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#### **Abstract**

Monoethanolamine solvent (MEA) is a common solvent used in biogas upgrading plant for carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S) removal. However, it has some downsides such as corrosive, high toxicity, and promotes products degradation. Alternatively, amino acid-based solvents such as potassium lysinate (LysK) have been found to have good absorption performance. It is also claimed to be more environmentally friendly as it is less toxic and has a good biodegradability. However, its actual environmental impact for the application of biogas upgrading has not been quantified in a detailed manner. Therefore, in this study, the environmental impact of LysK solvent is quantified from gate to grave in terms of Global Warming Potential (GWP), Acidification Potential (AP) and Eutrophication Potential (EP) using life cycle assessment (LCA) approach. The process was simulated using process simulator, SuperPro Designer version 10 to obtain the input-output data. LysK solvent has a low heat of absorption, which could result in lower CO<sup>2</sup> emissions during the biogas upgrading process. However, due to its energy-intensive nature, the incineration process significantly contributed to GWP, AP, and EP. There were also emissions of NO<sub>x</sub> and SO<sub>2</sub> from the flue gas of the incinerator. The findings of this research provide some insight on the environmental impact of utilising LysK for biogas upgrading.

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#### **Article Info**

Received 23 January 2022 Received in revised form 27 October 2022 Accepted 31 October 2022 Available online 2 December 2022

## Keywords

Life cycle assessment Global warming potential Acidification potential Eutrophication potential Potassium lysinate

#### 1 Introduction

Biogas is a well-established renewable energy resource produced from the bacterial breakdown of organic matter or feedstock by anaerobic microbes (methanogens) in the absence of oxygen (O<sub>2</sub>). It consists of 50 - 70% methane (CH<sub>4</sub>), 30 - 50% carbon dioxide (CO<sub>2</sub>) as main constituents and traces of other contaminants such as hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), carbon monoxide (CO), nitrogen (N<sub>2</sub>), siloxanes (Si) and volatile organic compounds (VOCs) (depending on the source of the feedstock) [1]. Biogas can be used to produce heat and electricity [2,3]. Biogas production process not only produce a sustainable energy source, but it also recycles organic waste into digested biomass that can be utilized as fertilizer and soil conditioner [1]. Therefore, biogas can be an alternative solution to the world's insatiable energy demands, valorizing waste and reducing the greenhouse gases (GHGs) emissions of CH<sub>4</sub> which has 25 times more adverse effects on global warming than CO<sub>2</sub> [4].

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While the main objective of the biogas industry is to reduce the reliance on fossil fuels, with the final goal of mitigating global warming [5], it has been widely acknowledged that, apart from CH<sub>4</sub>, the remaining components in biogas are undesirable and are regarded as impurities [1]. Some of the impurities may cause undesirable impacts, such as corrosion and hazards for human health [6]. Therefore, the impurities in biogas must be removed before it can be further utilized for heat or electricity generation. This process is known as biogas upgrading. Biogas with high CH<sub>4</sub> purity has the same properties as natural gas, especially in terms of heating value [7].

Currently, several technologies have been developed and commercialized for biogas upgrading, such as absorption (e.g., chemical scrubbing with amine and high-pressure water scrubbing), adsorption (e.g., pressure swing adsorption), membrane separation, and cryogenic separation [8-10]. Absorption is usually considered as a popular and successful approach for upgrading biogas among these technologies. This process has the advantage of being the most matured technology and has been commercialized for decades, as well as being suitable for retrofitting existing plants [11].

However, the negative environmental impact of the absorption process's exponential use of volatile and hazardous organic solvents has prompted the development of greener alternatives [12]. The common alkanolamines solvent used in the absorption process poses several issues such as high toxicity, corrosion, and the formation of degradation products [13]. Through the simulation using SuperPro Designer software, it was discovered that biogas upgrading using monoethanolamine (MEA) has the highest energy requirement for heating to regenerate CO<sub>2</sub> from rich amine solution, which could contribute to global warming [14]. Hence, the development of green solvents with unique combinations of properties and related techniques for targeted applications has attracted growing attention [15]. Amino acid-based solvents have recently emerged as an alternative solvent in the biogas upgrading process since their functional group is similar to that of alkanolamines but they present better absorption performance [16,17]. Solvents with amino acid salts (AASs) have low absorbent losses and greater resistance to oxidative degradation. They also have better biodegradability, which could lead to solvent disposal with lower environmental impacts [18].

Potassium lysinate (LysK) is among the amino acid-based solvents with good CO<sub>2</sub> absorption performance [19]. Despite the claim that it is a more environmentally friendly solvent compared to the traditional alkanolamine solvents, the environmental impact of LysK has not been clearly quantified thus far. Therefore, this study aims to evaluate the environmental impacts of LysK from gate to grave using the LCA approach. Specifically, the Global Warming Potential (GWP), Acidification Potential (AP) and Eutrophication Potential (EP) of LysK from the biogas upgrading process until its end-of-life were evaluated.

#### 2 Materials and methods

## 2.1 Goal and scope definition

The LCA was carried out based on ISO 14040 [20]. The main goal of this study is to analyse the environmental impact of LysK solvent from the biogas upgrading process (gate) to its end-of-life (grave). The functional unit (FU) is 1 kg/h of raw biogas. The raw biogas in this study was assumed to have been pre-treated for the removal of H<sub>2</sub>S before entering into the process at the system boundary. The quality of the final biogas, biomethane (bioCH<sub>4</sub>), should be a sufficient substitute for natural gas which is 99.05% CH<sub>4</sub>, 0.65% CO<sub>2</sub>, 0.17% N<sub>2</sub> and 0.13% O<sub>2</sub>. The molecular structure of LysK which was obtained by neutralizing the amino acid with potassium hydroxide (KOH) is shown in Fig. 1. KOH is an environmentally friendly inorganic substance as it does not contain degradable functional groups and thus has no detrimental impact on the biological oxygen demand in water, whereas amino acid has a high biodegradation potential and low toxicity [21].

Fig. 1 Molecular structure of potassium lysinate (LysK).



The system boundary of this study is shown in Fig. 2. Only processes inside the dotted line were considered for the assessment in this study. It included the biogas upgrading process where there was absorption of impurities from the raw biogas using the LysK solvent. The LysK solvent underwent solvent regeneration through desorption process with 30% being assumed to be recycled back into the absorption process while the remaining was sent for incineration as the end-of-life treatment of the waste solvent.

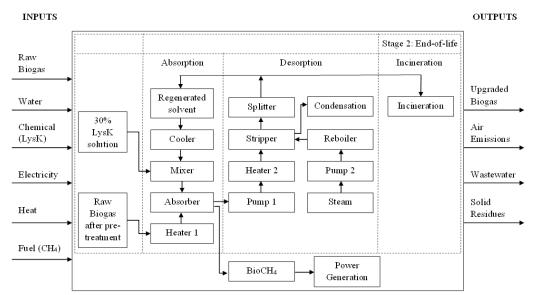


Fig. 2 System boundary of this study.

The transportation of the solvent from the production site to the biogas upgrading plant and the waste solvent to the end-of-life facility is not included in the scope of this study. It is because transportation is case-specific [22], and it is not recommended to use specific data to develop a generic estimate.

Furthermore, the processes involved in biogas production, such as anaerobic digestion, the biogas cleaning or pre-treatment of raw biogas, wastewater treatment (wastewater from the top of the stripper), and the end use of bioCH<sub>4</sub> are not accounted for in this study because the goal of this study is to evaluate the environmental impact of using LysK solvent for biogas upgrading. Therefore, only processes within the system boundary were taken into consideration.

## 2.2 Inventory analysis

The inventory data in this study was generated using process simulator, SuperPro Designer version 10. The composition of biogas was solely determined by the feedstock from which it was produced. The process simulation flowsheet of LysK solvent using SuperPro Designer is shown in Fig. 3. In this study, the biogas was assumed to be produced using a mesophilic anaerobic digestion phase (37 - 39 °C). The composition of biogas from the anaerobic digestion process was derived from literature [23-25] with an average value was chosen as shown in Table 1. The value of 250 m³/h of raw biogas was selected since it is a common flowrate in industrial applications [26]. The conversion of electricity generation from coal into specific amount of pollutants is shown in Table 2 [27,28]. Coal was assumed to be used in electricity generation so as to consider the worst-case scenario of pollutants generation.

Table 1 Composition of raw biogas produced in mesophilic anaerobic digestion [23-25].

Biogas flow	Temperature, ° C	Pressure,	Composition (Vol. %)				
rate, m³/h		bar	$\mathrm{CH_4}$	$CO_2$	$N_2$	$H_2S$	$O_2$
250	38	1	60	39.8	0.1	0.02	0.08

The assumptions and limitations for LysK solvent process used for the simulation process were the following:



- The simulation of the pre-treatments (granular activated carbon adsorption impregnated with NaOH) was performed in SuperPro Designer assuming H<sub>2</sub>S removal efficiency of 99% due to its high efficiency and fast reaction [29].
- A 30 wt.% LysK solution was used for the biogas upgrading. This concentration was selected because of the low regeneration energy.
- The amount of liquid solvent needed was optimized to the minimum amount that was required in the absorption column to achieve the final targeted biogas composition after the upgrading process. A smaller amount of liquid solvent supplied would reduce the efficiency of the column [30].
- The absorption column was simulated with CO<sub>2</sub> and H<sub>2</sub>S removal efficiency of 99% because the chemical solvent reacted selectively with CO<sub>2</sub> and H<sub>2</sub>S [31].
- The stripping column was assumed to have CO<sub>2</sub> and H<sub>2</sub>S stripping efficiency of 99% because the chemical bond between acidic gases (CO<sub>2</sub> and H<sub>2</sub>S) and LysK solution can be broken at the high temperature in the stripper [32].
- All carbon in the feed streams of the incineration process was converted to CO<sub>2</sub>, all hydrogen was oxidized to water, all nitrogen contained in combustible component was converted into gaseous NO<sub>x</sub>, all sulfur was converted to SO<sub>2</sub>, all phosphorous was converted to phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) and all ash content remained as ash [33].
- The alkali metal in the LysK solution was converted to ash in the incineration process [34].
- Electric heater was used to supply heat for the processes.
- Apart from SuperPro Designer, a multi-input allocation model was developed in incineration modelling [35].

Table 2 Conversion of electricity generation from coal into specific amount of pollutants [27,28].

Energy	<b>Parameters</b>	Quantity
1 MJ Electricity	СО	0.000041547 kg
	$NO_x$	0.000241317 kg
	$\mathrm{SO}_2$	0.000191455 kg
	VOC	0.000004794 kg
	CO <sub>2</sub>	0.180763 kg

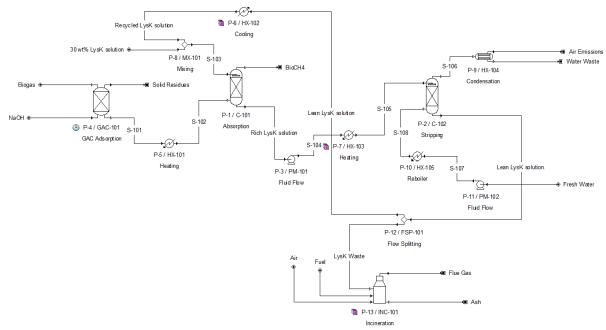


Fig. 3 Process flow diagram of LysK solvent for simulation in SuperPro Designer.



The operating condition of the absorber was 40 °C and 1 bar where the exothermic chemical reaction occurred while the stripper acted as a regeneration column at 103 °C and 1.5 bar. The condenser was operated at temperature of 31.1 °C which was above critical temperature of CO<sub>2</sub> and pressure remained unchanged [36]. It was decided that 70 % of the LysK waste was purged and the remaining 30 % was recycled. The residence time of the LysK waste was at a minimum of 2s with temperature of 1200 °C to achieve complete combustion. In incineration, the fuel used was methane gas while the oxygen source was air (76.71% N<sub>2</sub> and 23.29% O<sub>2</sub>) [35].

In the SuperPro Designer software, the relevant unit processes were selected, put in sequence and the streamlines were connected. After inserting all the necessary data into the software, the power consumption and the emission of pollutants were traced from the generated datasheet.

#### 2.3 Impact Assessment

The purpose of impact assessment is to convert and aggregate the result of inventory analysis into environmentally relevant indicator. It can be explained as transformation of inventory results into number of contributions to environmental impact categories such as GWP, AP and EP. Each of the identified environmental potential indexes were evaluated using the expressions summarized in Table 3. The main parameters used in the formula are the mass (m<sub>i</sub>) in kilogram (kg) of the specific considered pollutant released to air as well as the pollutant specific weighting factors (GWP<sub>i</sub>, AP<sub>i</sub> and EP<sub>i</sub>) representative of the environmental effect potential per mass unit of the specific considered pollutant.

Table 3 Selected environmental effect potential indexes definitions and respective units of measure [20].

Index	Formula	<b>Unit of Measure</b>
Global Warming Potential	$GWP = \sum GWP_i \times m_i$	kg CO <sub>2</sub> equivalent (kg CO <sub>2</sub> -eq)
Acidification Potential	$AP = \sum AP_i \times m_i$	kg SO <sub>2</sub> equivalent (kg SO <sub>2</sub> -eq)
<b>Eutrophication Potential</b>	$EP = \sum EP_i \times m_i$	kg PO <sub>4</sub> <sup>3-</sup> equivalent (kg PO <sub>4</sub> <sup>3-</sup> -eq)

Each of the environmental potential index was calculated as the sum of the effects of multiple pollutants, where each pollutant mass was multiplied with its specific weighting factor. These weighting factors are denoted by a reference substance. This enables direct comparison and summarization of the effects of multiple and unrelated pollutants [37]. The considered specific weighting factor values for the selected pollutants are listed in Table 4. The data in Table 4 illustrate that the weight of various pollutants might vary, and the selected pollutants are divided into two categories: power consumption and process emissions.

Table 4 List of specific weighting factors for the pollutants [20].

	Sources		GWPi	APi	EPi	
Pollutant	Power Consumption	Emissions	(kg CO <sub>2</sub> eq./kg)	(kg SO <sub>2</sub> eq./kg)	(kg PO <sub>4</sub> <sup>3-</sup> eq./kg)	
CO	$\sqrt{}$		2	0	0	
NOx	V	$\sqrt{}$	0	0.7	0.13	
$SO_2$	$\sqrt{}$	$\sqrt{}$	0	1	0	
VOC	$\sqrt{}$		3	0	0	
$CO_2$	$\checkmark$	$\sqrt{}$	1	0	0	
H <sub>2</sub> S		V	0	1.88	0	
NH <sub>3</sub>		<b>√</b>	0	1.88	0.35	

For a general case of solvent from the use-phases to the end-of-life treatment, the total amount of each considered potential index can be calculated, once the pollutant mass emissions are specified, using the expression reported in Table 3 and the specific weighting factors of Table 4.

## 2.4 Data Interpretation

The interpretation is the final phase of an LCA which considers and analyses the results of the previous phases in the light of the uncertainties of the applied data and the assumptions that have been made and documented throughout the study. In this study, three steps were involved in the data interpretation. Firstly, the significant issues (key processes and assumptions, most relevant elementary flows) from the other phases of the LCA were identified. Secondly, these issues were assessed in terms



of their impacts on the LCA's overall outcomes. Lastly, the evaluation's findings were incorporated into the study's conclusions and recommendations [38]. The findings from this work were also compared to those of other similar studies for validation [39].

#### 3. Results and discussion

## 3.1 Environmental Impact of LysK Solvent

Fig. 4 shows the environmental impacts associated with the biogas upgrading (Stage 1) and the end-of-life (Stage 2) for LysK solvent based on the emission data generated from the simulation process in this study. A lower amount of GWP, AP and EP was observed in the absorption process. This was because only traces of CO<sub>2</sub>, CO, VOC, NO<sub>x</sub> and SO<sub>2</sub> were emitted as a result of lower electricity consumption in the absorption process among the other processes. In addition, the treated gases such as CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> leaving from the top of the absorber were stored for power generation.

With respect to the bioCH<sub>4</sub> generation process using 30 wt.% LysK solution, it was observed that electricity related to the high demand of energy in the desorption process was responsible for the high impact of GWP compared to absorption process. Biogas upgrading by 30 wt.% of LysK solution was expected to use less electricity in the desorption process. Although the reboiler temperature influences the solvent's regeneration level, with higher reboiler temperatures resulting in higher regeneration levels, which are closely related to the cyclic loading of the solvent, 30 wt.% LysK solution with a lower heat of absorption has greatly reduced the regeneration energy use. However, the increase in the reboiler temperature in the desorption process which was responsible for most of the electricity consumptions has contributed to the higher amount of GWP as compared to the absorption process due to the main emissions of CO<sub>2</sub> with traces of VOC and CO emissions. Furthermore, the biogenic CO<sub>2</sub> entrapped in the stripper to be released back into the atmosphere had a notable impact on GWP in the desorption process.

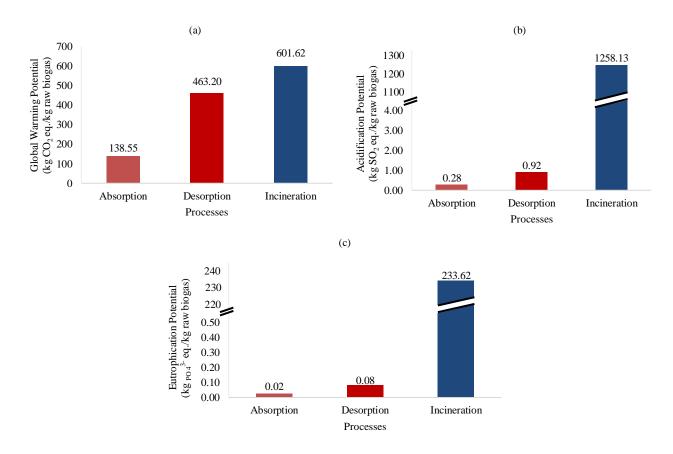


Fig. 4 (a) GWP (b) AP, and (c) EP of 30 wt.% LysK solution.



On the other hand, the increase in the reboiler temperature has caused AP and EP impact to some extent to be clearly visible in the desorption process. Similarly, an additional emission of traces of H<sub>2</sub>S leaving the stripper [40] as a result of high removal efficiency by using activated carbon impregnated with NaOH contributed the least in the desorption process and it also represented the lowest of the total contributions to AP in the desorption process. According to Hook [41], van Holst et al. [42] and Weiland et al. [43], LysK shows good resistance to oxidation. In addition, the thermal degradation of LysK solvent is a very slow process, so there is a low possibility for product degradation and hence no environmental or toxic issues [36].

The incineration process posed a higher environmental impact in terms of GWP, AP and EP, compared to absorption and desorption processes. Waste solvent incineration process breaks down the element composition of all chemical components that are present in the feed streams, allowing reactions between the most volatile components of the waste with the O<sub>2</sub> and N<sub>2</sub> in air [44]. The amount of emitted CO<sub>2</sub> is proportional to the carbon composition (mass %) of the waste LysK solvent [35]. As shown in Fig. 1, the LysK solvent had a high carbon composition (mass%). This contributed to a high amount of CO<sub>2</sub> being emitted from the waste solvent incineration process into the environment based on the simulation results, hence the high GWP value in the incineration process. In addition, the high electricity consumption significantly increased the GWP impact of the incineration process. It is worth noting that the electricity consumption was dependent on the mass of the waste LysK solvent. Therefore, increasing the amount of waste LysK solvent directed to the incinerator would increase the impact of GWP [35].

On the other hand, NO<sub>x</sub> contributions were associated with the combustion of nitrogen compounds in the waste LysK solvent during the incineration process. AP was mainly associated with the emissions of SO<sub>2</sub> and NO<sub>x</sub> while EP was associated with NO<sub>x</sub> emissions in the incineration process. However, more than 85 percent of the energy in the waste solvent could be converted into heat, which could then be used to produce superheated steam in a steam boiler for turbine-based electrical power generation [45]. Therefore, it was expected that a lower amount of NO<sub>x</sub> and SO<sub>2</sub> were emitted due to lower energy consumption in the incineration process compared to desorption process. For the electricity consumption, the desorption process was observed to be having the highest values, followed by the incineration and absorption process. Although there is presence of alkali metal in the LysK solution, it was converted to ash during the incineration process which was then sent to a secure landfill for final dumping.

In short, it was concluded that the overall environmental impact of the LysK solvent was associated with CO<sub>2</sub>, VOC, CO, NO<sub>x</sub> and SO<sub>2</sub> emissions as a result of high electricity consumption in both biogas upgrading and incineration process, as well as additional emission of CO<sub>2</sub> and traces of H<sub>2</sub>S from the stripper and NO<sub>x</sub> and SO<sub>2</sub> from flue gas of the incinerator with AP having the highest values, followed by GWP and EP. When compared to other solvents, it was found that biogas upgrading using MEA has the highest energy requirement for heating to regenerate CO<sub>2</sub> and H<sub>2</sub>S from rich amine solution, which has contributed to the higher amount of GWP as compared to LysK [14]. According to Zhao et al. [36], LysK solution has lower heat of absorption (about 55 - 70 kJ/mol) compared to 30 wt.% MEA solution (about 80 - 85 kJ/mol). This translates into lower regeneration energy required for LysK solution. However, 30 wt.% LysK solution showed faster absorption kinetics, resulting in more stable carbamate. Therefore, it is not unexpected that increasing heat of absorption can be observed [46]. Although the removal efficiency of 30 wt.% MEA solution is higher, it shows low cyclic CO<sub>2</sub> and H<sub>2</sub>S loading between the absorber and stripper [47]. Therefore, the stripper acts as a regeneration column at 120 °C and 1.5 bar for enhancing the removal efficiency.

## 3.2 Potential of Optimization using Heat Integration

Since heat requirement was identified as the main contributors to energy consumption in the process, optimization of the process with heat integration network was conducted to investigate its potential in reducing the GWP, AP and EP. Fig. 5 shows a heat exchanger network (HEN) in the biogas upgrading process. Table 5 shows the comparison of overall GWP, AP and EP results with and without the integrated HEN. It was found that the process has a lower GWP with the integration of HEN. The reduction of AP and EP was not significant with the HEN because most of the pollutants contributing to AP and EP was from the incineration process. Therefore, for AP and EP, the reduced environmental impact was not significant with the integration of HEN.



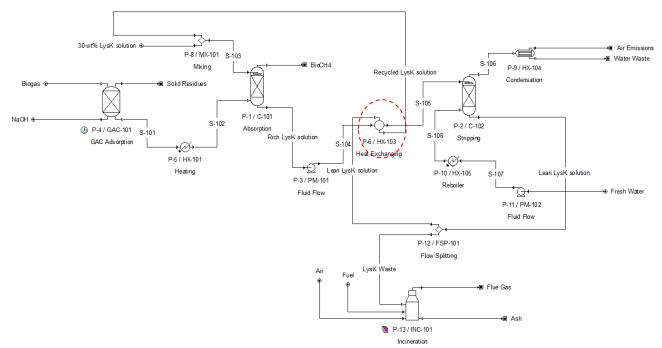


Fig. 5 Process flow diagram after heat integration.

Table 5 Overall GWP, AP and EP for LysK solvent (with and without HEN).

Impact Categories	Without HEN	With HEN
Global Warming Potential (kg CO2 eq./kg raw biogas)	1203.38	926.27
Acidification Potential (kg SO <sub>2</sub> eq./kg raw biogas)	1259.33	1258.78
Eutrophication Potential (kg PO4³- eq./kg raw biogas)	233.72	233.67

## 4. Conclusions

The GWP, AP and EP of LysK solvent was successfully evaluated using LCA with data obtained from process simulator. The incineration process contributed the highest GWP, AP and EP due to its energy-intensive nature and additional emissions of NO<sub>x</sub> and SO<sub>2</sub> from flue gas of the incinerator. However, LysK solution has a lower heat of absorption which translated into lower regeneration energy required for LysK solution and resulted in a reduction in CO<sub>2</sub> emissions in the biogas upgrading process. The overall result showed that LysK solvent has GWP with 1203.38 kg CO<sub>2</sub> eq per kg raw biogas, AP of 1259.33 kg SO<sub>2</sub> eq per kg raw biogas and EP of 233.72 kg PO<sub>4</sub><sup>3-</sup> eq per kg raw biogas. For future work, it is suggested that the process model data be evaluated on a lab or pilot size to ensure that the implementation is feasible and achievable.

## Acknowledgement

This research was jointly funded by Universiti Teknologi PETRONAS via the Joint Research Project (JRP8) funding, Universiti Teknologi Malaysia via Matching Grant (PY/2021/00347 & PY/2021/00272) and Universiti Malaysia Perlis (Grant No: 9023-00022).

## **Declaration of competing interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



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