Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Cryogenic vs. absorption biogas upgrading in liquefied biomethane production – An energy efficiency analysis



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ARTICLE INFO

Keywords: Liquefied biomethane Cryogenic upgrading Chemical absorption upgrading Methane utilization

ABSTRACT

Production of liquefied biomethane (LBM) from biogas comprises two major energy intensive processes; upgrading to increase the methane concentration and refrigeration to liquefy the upgraded biogas. Amine-based absorption has been considered an attractive option for biogas upgrading in industrial applications. The temperature increase associated with amine regeneration is, however, in conflict with the cooling requirement of the subsequent liquefaction process. Hence, cryogenic biogas upgrading, integrated with liquefaction, has emerged as an interesting alternative.

In this paper, a rigorous energy analysis was performed for comprehensive models of the two aforementioned LBM production alternatives. Both processes were modeled using Aspen HYSYS* and optimized to minimize the energy use. The results indicate that the integrated cryogenic upgrading process is favorable in terms of both overall energy efficiency and methane utilization. Moreover, the energy analysis implies that the liquefaction process accounts for the major part of the energy input to an LBM plant, demonstrating the significance of improving the energy efficiency of the liquefaction process in order to improve the overall performance of the LBM process.

1. Introduction

The use of fossil fuels in the transportation sector has remained dominant although renewable energy sources being introduced in the energy market. According to a recent report from the Renewable Energy Policy Network for the 21st century [1], the global renewable share of total energy use was 20.5% in 2016. However, the permeation of renewable energy in different sectors is not identical; for instance: energy use in the transportation sector comprises 32% of the total energy use in the world, out of which renewable energies like biofuels and renewable electricity account for only 3.1% [1].

Lately, liquefied biomethane (LBM) from biogas has attracted much interest as an alternative fuel [2]. Similar to liquefied natural gas (LNG), the energy density of LBM is about 21 MJ/L, which is approximately 2.4 times higher than that of compressed biomethane (Bio-CNG) [3]. The higher energy density of LBM makes it feasible as long distance transportation fuel. Currently, the global LBM production is limited to only 43,100 tonnes per annum, which is considerably lower than global trade of liquefied natural gas (LNG) with 293.1 million tonnes in 2017 [4]. However, it is estimated that demands for LBM will increase not only for the vehicle transportation sector, but also in maritime transport over the next decades [4].

As a downstream product of biogas production plants, LBM production requires two energy intensive processes: upgrading and liquefaction. Biogas produced through either an anaerobic digester or landfill must be upgraded in order to increase the methane (CH₄) concentration (i.e. increase the heating value of the biogas) and remove harmful impurities in the final product. The upgraded biogas is known as biomethane, which contains mainly CH₄. Typical biogas compositions and LBM purity requirements are presented in Table 1. Based on the purpose of biogas utilization, one or a combination of conventional upgrading technologies such as water scrubbing, chemical absorption, pressure swing adsorption, or membrane separation can be applied [5].

In order to produce applicable biomethane in liquid form, the obtained biomethane from the upgrading processes must be liquefied in an external refrigeration cycle. Knowledge regarding refrigeration cycles is mature in terms of process design and energy optimization since it has been implemented in LNG plants for the past 100 years [6-8]. Cascade liquefaction processes, mixed refrigerant processes, and expander liquefaction processes (i.e. reverse Bryton cycles) are commercialized for liquefaction purposes [9].

In advance of performing a comprehensive energy assessment of

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https://doi.org/10.1016/j.fuel.2019.01.172

Received 29 September 2018; Received in revised form 13 January 2019; Accepted 30 January 2019 Available online 21 February 2019

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Table 1Typical biogas composition and LBM specification [10,11].

Compound	Unit	Anaerobic Digestion	Landfills	LBM purity requirement
$\begin{array}{c} CH_4\\ CO_2\\ H_2S\\ H_2O\\ N_2\\ H_2\\ O_2 \end{array}$	mol% mol% ppm mol% mol% mol%	50-70 19-38 72-700 < 0.6 0-5 NA 0-1	45–62 24–40 15–427 NA 1–17 NA 1–2.6	> 99.99 < 10 ⁻³ < 3.5 < 5·10 ⁻⁵
Siloxane Total chlorines	ppm mg/Nm ³	trace 100–800	NA NA	

different LBM production plants in this paper, an overview regarding energy use of different biogas upgrading methods and liquefaction processes is provided in order to highlight advances and with respect to energy use.

1.1. Biogas upgrading

To date, a number of studies have focused on the energy aspects of different biogas upgrading methods. Rotunno et al. [12] simulated a pressurized water scrubbing process considering a biogas mixture of 60 mol% CH₄ and 40 mol% CO₂. They reported that a purity of 98.1 mol % CH₄ was obtained at 10 bar and 25 °C, which is suitable for gas grid injection and bio-CNG production. They stated that the energy efficiency of the upgrading plant producing biomethane with quality of gas grid injection was 89.8%. Budzianowski et al. [13] considered various configurations of water scrubbing and water regeneration for a biogas mixture of 65 mol% CH₄ and 35 mol% CO₂. Their results indicated that a specific energy use of 0.32 kWh/Nm³ of raw biogas was required to produce biomethane with a purity of 98 mol% CH₄, which was equivalent to 15.2% of the energy content of the raw biogas.

Haider et al. [14] simulated different types of membrane operating at different pressure for a mixture of CH_4 and CO_2 containing 50–70 mol% CH_4 . They stated that polyimide membranes in three stages upgraded the biogas up to 97 mol% CH_4 with specific energy of 0.22 kWh/Nm³ of raw biogas. Iovane et al. [15] conducted experimental studies considering a biogas composition including H₂S and other trace elements with polymeric membranes. They reported that the purity of biomethane reached 99 mol% CH_4 when the feed gas pressure was increased to 25 bar. Valenti et al. [16] investigated various designs for cellulose acetate membranes at 26 bar in order to upgrade a mixture of 55 mol% CH_4 and 45 mol% CO_2 . They reported that a specific energy use from 0.33 to 0.47 kWh/Sm³, depending on the design, was required to achieve purity of 97 mol% CH_4 .

An overview of literature indicates that upgrading biogas to high quality biomethane, satisfying the purity requirements for LBM production, hardly can be achieved only through water scrubbing or membrane separation [17]. Thereby, a polishing step should also be considered. Although the polishing step is costly and essential for achieving high quality biomethane, the specific energy requirement of the polishing step has not been fully considered in literature.

Pressure swing adsorption (PSA) is a technology that can be used for both upgrading and polishing [4]. Ferella et al. [18] performed experiments for low pressure PSA with different sorbents such as zeolite and activated carbon. They reported that biomethane with a purity of above 98 mol% CH₄ and a methane loss of 5% obtained using synthesized zeolite from fly ash. Augelletti et al. [19] simulated a novel twostage PSA configuration that upgraded a biogas mixture of 60 mol% CH₄ and 40 mol% CO₂. They demonstrated that a biomethane stream with a purity of above 97 mol% CH₄, and CO₂ with a purity of up to 99.4% were obtained from the novel configuration, while the required specific energy and methane loss were 0.35 kWh/kg of biomethane and about 3%, respectively. Recently, Liu et al. [20] simulated a vacuum swing adsorption process for three-step adsorption beds and obtained CH₄ purity of 99.4 mol% from a feed gas of 50 mol% CH₄ and 50 mol% CO₂. Their simulation showed a specific energy requirement of 0.22 kWh/kg of biomethane and biomethane recovery of 96.9%. Although the LBM requirements can be satisfied, high methane loss remains a challenge with PSA.

Amine-based absorption is suitable not only for large industrial scale applications, but also for obtaining the targeted LBM specifications without requiring additional polishing steps [4]. The energy requirement for chemical absorption consists of work for biogas compression and heat at high temperature in range of 100–130 °C for amine regeneration in a stripper column [21]. It is worth mentioning that the type of amine has great impact on the energy use in chemical absorption. For instance, biogas upgrading using monoethanolamine (MEA) requires more heat to regenerate the amine in stripper column than Methyl diethanolamine (MDEA) [22]. However, while the operating pressure is in the range 3–8 bar when using MEA, a pressure range of 45–70 bar is required for MDEA, depending on the purification requirements [22,23]. This means that a smaller amount of work is required for biogas compression prior to the absorber column with MEA than with MDEA.

Vo et al. [24] evaluated chemical absorption with MEA for biogas upgrading. They demonstrated that approximately 2.5 kWh/m^3 of biomethane was required in the form of electricity and steam in order to obtain biomethane with 96 mol% CH₄. Most of the research concerning chemical absorption was focused on how to reduce the heating duties in the reboiler. For instance, Nejat et al. [23] showed that the reboiler heat duty reduced by approximately 47% once MDEA was substituted with a mixture of MDEA and Sulfolane.

In another study, Pellegrini et al. [25] investigated the energy requirement for LBM production from a biogas mixture of 60 mol% CH_4 and 40 mol% CO_2 . They evaluated MEA absorption as upgrading method in order to reach the LBM purity requirements, considering an external refrigeration duty for liquefaction. They found that about 29% of the methane available in the raw biogas stream would be consumed if the process was to be self-supplied with work and heat, considering conventional engineering processes. The results indicated that biogas upgrading accounted for 57.4% of the total energy requirement.

 CO_2 removal through chemical absorption is an exothermic reaction, which leads to an increase of biomethane temperature leaving the column. This is in conflict with the cooling duty for subsequent liquefaction process. Therefore, a comprehensive simulation model including both absorption-based upgrading and liquefaction assists in determining the actual energy use and potential improvements.

In addition to the aforementioned upgrading methods, cryogenic separation in distillation columns has attracted much attention [5,26]. In cryogenic separation, the difference in boiling point for the various gas components is exploited to separate the components [27]. Obtaining high CH_4 content and CO_2 recovery account as advantages of this technology. Moreover, cryogenic separation reduces the cooling requirement in LBM production since biogas upgrading takes place at lower temperature.

Yousef et al. [28] proposed a one-stage distillation column for a biogas mixture of 60 mol% CH_4 and 40 mol% CO_2 that purified biomethane up to 94.5 mol% CH_4 and obtained a CO_2 stream with a purity of 99.7 mol% as by-product. In a successive study [29], they employed two distillation columns operating above and below the critical pressure of pure CH_4 , respectively, in order to upgrade biogas up to 97 mol% of CH_4 . When considering heat recovery in the process design, the specific energy requirement was reduced to 0.25 kWh/Nm³ of raw biogas for producing liquefied CO_2 with purity of 99.7 mol% at 110 bar and biomethane with purity of 97.1 mol% CH_4 at 5 bar [29].

Lange et al. [22] proposed dual-pressure distillation columns, with one column operating at high pressure as a stripper section without condenser and one column operating at lower pressure as an enrichment section without reboiler. They concluded that the use of low temperature separation technologies was advantageous, compared to a conventional MDEA absorption, when the CO₂ concentration in the feed gas was high. In successive studies [25,30], they simulated various types of cryogenic separation concepts including the Ryan-Holmes process [31,32], an anti-sublimation process [33,34] and dual-pressure distillation columns. Refrigeration cycles were not included in their simulation. The results indicated that approximately 14% of the methane in the raw biogas would be consumed if the process with dualpressure distillation columns was supposed to be self-supplied with work and heat, which was half of the methane consumption for chemical absorption upgrading. Furthermore, their simulations showed that nearly 22% of the methane in the raw biogas was consumed for a synergetic process including anti-sublimation separation and liquefaction. Baccioli et al. [35] simulated a small-scale LBM production plant applying the anti-sublimation process for upgrading and a dual-expander refrigeration cycle for liquefaction. For a biogas mixture with 40 mol% CH₄, 59 mol% CO₂ and 0.5 mol% of H₂S and 0.5 mol% H₂O, the specific energy requirement was 1.45 kWh/kg of LBM in order to produce LBM with a purity of 97 mol% CH₄

1.2. Biogas liquefaction

In conventional approaches, the high quality biomethane obtained from the upgrading is cooled down through a separate liquefaction unit in order to produce LBM. Birgen and Jarque [36] performed simulation using Aspen PLUS^{*} for liquefying biomethane generated from an upgrading process with a production capacity of 100 MW_{LHV} of LBM. They showed that the total power requirement for a single expander liquefaction process was about 12.4 MW. Baccioli et al. [35] simulated a dual-expander liquefaction process for small-scale LBM production. Results from their simulation indicated that 0.75 kWh/kg LBM was required for liquefaction process.

In comparison with biogas upgrading, biomethane liquefaction has received limited attention in the literature.

1.3. Objective

Despite existing research regarding LBM production, few studies have focused on optimization of different design variables affecting the total energy use of the LBM production plants. This paper aims to develop comprehensive models of two different process configurations by simulating and optimizing the complete processes, including both upgrading and liquefaction. In the present paper, a cryogenic gas separation process integrated with liquefaction is compared with a conventional approach of LBM production through chemical absorption followed by liquefaction. Models have been developed in Aspen HYSYS^{*} V9.0 considering a common raw biogas composition. Additionally, the design variables are optimized with respect to energy use. The performance of the two configurations is evaluated by means of energy analysis in order to identify potential improvement.

The layout of the paper is as follow: In Section 2, descriptions of the two process models are presented. The methodology of the optimization procedure and energy efficiency calculations are provided in Section 3. Results from the energy simulation and energy analysis are presented in Section 4. In Section 5, conclusions and suggestions for future work are presented.

2. Process descriptions

Two different approaches of producing LBM have been studied in this paper:

- Case 1: Cryogenic separation integrated with liquefaction in a synergetic approach
- Case 2: Amine-based absorption with subsequent liquefaction in a

conventional approach

In case 1, cryogenic separation is integrated with the liquefaction process. In case 2, an amine-based absorption upgrading followed by a liquefaction unit is considered. Identical feed and product conditions are applied for both processes. The raw biogas stream consists of 60 mol % CH₄, 39.9 mol% CO₂ and 0.1 mol% H₂S at 35 °C and 1 atm. Liquefied biomethane (LBM) and liquefied CO₂ (LCO₂) are considered as final product and byproduct of the LBM production plant, respectively. The CO₂ content should be below 50 ppm for the LBM stream and above 99.7 mol% for the LCO₂ stream. Moreover, all the H₂S from the raw biogas leaves the LBM production plant with the LCO₂ stream.

In general, raw biogas generated from a biogas production plant contains water (see Table 1). Depending on the type of biogas upgrading method, dehydration can be accomplished before or after the upgrading step. For instance, removal of water in a cryogenic gas separation is carried out before the upgrading step. For upgrading based on chemical absorption, the dehydration unit is placed after the upgrading step, as the amount of water removal depends on the water content at the outlet of the absorber. In this study, it is assumed that the raw biogas does not contain water, or alternatively is removed prior to upgrading. Therefore, no dehydration unit was considered for case 1, while a dehydration unit was considered for case 2 due to water being present during the chemical absorption upgrading.

It is assumed that the water from the biomethane stream and the high content CO_2 stream, respectively, from the outlet of the absorber and the outlet of the stripper in case 2 is removed using tri-ethylene-glycol (TEG) absorber/regeneration columns. The energy requirement of the dehydration process is mainly due to TEG regeneration, which involves heat at elevated temperature in the reboiler [37,38]. In the present study, the energy costs of the dehydration are estimated in accordance with the work by Kinigoma [39]. Furthermore, in accordance with recommendations from Aspelund et al. [40], the processes have been designed in such a way that cooling duties are delivered at high pressure. Therefore, an expander is placed at the end of LBM stream in order to adapt the pressure and temperature levels to the final LBM conditions.

2.1. Cryogenic upgrading scheme (case 1)

The flow sheet of an integrated cryogenic upgrading process for LBM production is given in Fig. 1. Biogas upgrading is accomplished at high pressure by means of two cascading distillation columns operating at different pressure level. Besides the columns, the model consists of a gas compression unit and one expander. Cooling is provided by a single expander refrigeration cycle with nitrogen, which is coupled to the upgrading process.

Initially, a high pressure raw biogas stream (S101) is produced by passing through the compression unit. After leaving the compression unit, the raw biogas (S102) is precooled in a multi stream heat exchanger (HX1) before entering the high-pressure distillation column (D1). CO_2 exits from the bottom as a liquid with a small amount of CH_4 and H₂S (S104). The top product (S103) of D1 passes through a valve (V1) producing a low-pressure stream (S105) that goes into the lowpressure distillation column (D2). In D2, biomethane with a CO₂ content below 50 ppm and without H_2S leaves from the top (S106). The stream with high concentration CO2 and H2S (S107) departs bottom of D2 in liquid form towards pump (P1) in order to increase the stream pressure (S108) before mixing with S104 in liquid mixer (M1). Liquefied CO₂ leaves M1 as a byproduct of the LBM production plant. The biomethane (S106) from the top of D2 is further cooled in a multi stream heat exchanger (HX2) followed by an expander (E1) in order to produce the final liquefied biomethane (LBM).

Data for both distillation columns are presented in Table 2. A sensitivity analysis is performed to select the number of theoretical trays for the two columns, in order to minimize the cooling duties in the



Fig. 1. Flow sheet of a cryogenic upgrading scheme (case 1).

Table 2						
Distillation	columns	data for	case 1	and	case 2.	

	Case 1	Case 1			
	High pressure distillation	Low pressure distillation	Absorber	Stripper	
Number of stages	20	22	25	20	
Column diameter (m)	1.5	1.5	3	3	
Feed stage no. (from top)	10	13	-	12	
Pressure (bar)	50.5	39.5	47	2.5	
Condenser temperature (°C)	-70.3	-87.8	-	35	
Reboiler temperature (°C)	13.8	4.1	-	130	
Reflux ratio	2.5	4.1	-	2	

condensers of the distillation columns, yet still comply with the LBM specifications. The high- and low-pressure distillation columns have 20 and 22 theoretical trays, respectively. The feed gas is introduced at the 10th stage and 13th stage in the high- and low-pressure distillation columns, respectively.

The heat duties are delivered to the reboilers in the high- and lowpressure distillation columns by heat from the cooling-water heat exchangers. The cooling requirements in the condensers of the distillation columns are provided by a single expander refrigeration process. The refrigeration cycle includes two multi-stream heat exchangers, one gas compression unit and one expander. The first multi-stream heat exchanger (HX1) provides the cooling requirement of the condensers of the distillation columns, whereas the second multi-stream heat exchanger (HX2) liquefies the biomethane. The high pressure nitrogen (S202) is obtained from the gas compression unit. By passing through HX1, the compressed nitrogen is precooled (S203). The precooled nitrogen passes an expander (E2) to produce a cold stream (S204). The cold stream is returned to the initial state (S201) entering the gas compression unit in a closed refrigeration loop after delivering cooling requirements in HX1 and HX2.

2.2. Chemical absorption upgrading scheme (case 2)

A complete model of a chemical absorption process followed by a liquefaction unit is demonstrated in Fig. 2. The model contains several sub-processes such as gas compression with intercooling, CO_2 and H_2S removal in an absorber, amine regeneration in a stripper column, dehydration units and a single expander refrigeration cycle with nitrogen. MDEA with a concentration of 45 wt% is selected as chemical solvent in order to take advantage of high pressure biomethane production with less heat requirement in the reboiler of the stripper column [23].

Compressed raw biogas (S101) leaves the compression unit and enters the bottom of the 25-tray absorber column (A1). Meanwhile, a lean amine solution (S102) at the same pressure as the feed gas enters the top of A1 in order to interact counter-currently with the raw biogas. The temperature of the lean amine solution is chosen to be 10 °C higher than the temperature of compressed raw biogas in order to facilitate the chemical reaction between CO₂ and MDEA as recommended by Lange et al. [22]. A rich amine solution (S104) flows from bottom of the absorber towards an expansion valve (V1) in order to reduce pressure of the rich amine solution (S105). An intermediate heat exchanger (HX1) is employed for transferring heat from the hot lean amine streams (S109 and S110) to the cold rich amine streams (S105 and S106). After recovering heat in HX1, the rich amine solution (S106) is introduced to a stripper column (S1), from which a high content CO₂ stream (S107) is extracted at the top.

Characteristics of the absorber and stripper columns are given in Table 2. The regenerated amine solution (S108) from the bottom of S1 is sent to a pump (P1) in order to set the same pressure as of A1. It is worth mentioning that an increase in MDEA pressure is necessary to achieve a higher level of gas separation in the absorber column. The loss of MDEA and water in the process is compensated by a make-up



Fig. 2. Flow sheet of a chemical absorption upgrading scheme (case 2).

unit followed by a cooling-water heat exchanger (HX2) adjusting the temperature of the lean-amine solution to the required temperature in the absorber. The make-up of MDEA and water is controlled by the temperature of the condenser (cond) in S1 [22]. Therefore, after performing a sensitivity analysis with respect to the amount of the required MDEA make-up and condenser duty, the condenser temperature was selected to be 35 $^{\circ}$ C.

A dehydration unit (DH1) processes the stream with high CO_2 concentration (S107) from the top of the stripper in order to produce a dry stream (S112). Then the dehydrated CO_2 stream is pressurized in a compression unit and further is cooled down in a multi-stream heat exchanger (HX3) producing a stream of liquefied CO_2 (LCO₂), which contains all the H₂S.

Upgraded biogas (S103), which is saturated with water, leaves top of the absorber at 45 $^{\circ}$ C towards a dehydration unit (DH2) in order to produce a dry biomethane stream (S114) before being liquefied through a single expander refrigeration process and an expander (E2).

For the single expander refrigeration process, nitrogen is compressed in a compression unit before precooling in the first multi-stream heat exchanger (HX3). The pressure is then reduced in an expander (E1) in order to supply adequate cooling duty for both multi-stream heat exchangers (HX3 and HX4). HX3 provides cooling duty for precooling the nitrogen, biomethane and CO_2 while HX4 is used to sub-cool the biomethane. The pressure of the biomethane is reduced to 1 atm through an expander (E2) producing LBM.

3. Methodology

3.1. Process modeling

The complete processes are simulated with the commercial process simulator Aspen HYSYS^{*} V9.0. In order to characterize the phase behavior of the mixtures that are involved in this study, two different thermodynamic models were selected from the Aspen HYSYS^{*} property selections. In accordance with the thermodynamic modeling validation by Lange et al. [22], the Soave-Redlich-Kwang (SRK) equation of state is used for the cryogenic upgrading scheme and refrigeration cycles, whereas the "acid gas - chemical solvent" package, as recommended by Aspen Technology [41], is employed for the chemical absorption upgrading scheme. In addition, the following assumptions are considered for both configurations:

- The pressure drop in coolers, heat exchangers, distillation columns and dehydration units are negligible.
- An identical isentropic efficiency of 80% is considered for compressors, expanders and pumps.
- Minimum temperature approach in the multi stream heat exchangers of the refrigeration cycles is 2 °C.
- Inlet and outlet temperature of cooling-water in heat exchangers are 20 and 25 °C, respectively.
- Gas compression units contain four stages of compressors with identical pressure ratio and intercooling to 35 °C.

Moreover, the CO_2 freeze-out utilization tool in Aspen HYSYS^{*} is employed to ensure that CO_2 ice is not forming during LBM production [42].

3.2. Process optimization

In order to ensure that the two studied configurations are run at a minimum energy requirement to produce the LBM, the processes are optimized using an exhaustive search method [43]. In this method, a number of combinations of the values of independent variables is examined through Aspen HYSYS^{*} and results are then analyzed using spreadsheets with respect to optimization constraints. The optimization procedure is performed for the two proposed configurations, in which the raw biogas consisted of 60 mol% CH_4 , 39.9 mol% CO_2 and 0.1 mol% H_2S .

A two-step successive optimization procedure is considered for case 1. In the first step, the total cooling duty of the upgrading step is minimized, which includes the cooling requirement in the condensers of the columns, precooling of the raw biogas in HX1 and sub-cooling the biomethane in HX2. The second step minimizes electrical work that is needed for the liquefaction process. The optimization problem for case 1 corresponding to Fig. 1 is formulated in Table 3.

The optimization procedure for case 2 includes a three-step approach in which the absorber column, the stripper column and liquefaction process are treated separately. The objectives of the optimization problem are to minimize the heating duty in the reboiler and the

Table 3

Optimization problems and design variables ranges for the cryogenic upgrading scheme (case 1).

Upgrading (step 1)			Liquefaction (step 2)		
Objective Constraints	min {Q _{precooling} + Q _{cond1} - CO ₂ content in LBM - CH ₄ loss < 1 mol% - No H ₂ S content in LBM	+ Q _{cond2} + Q _{subcool} } < 50 ppm	Objective Constraints	min { $W_{N2 \text{ compression}} - W_{E2}$ } Minimum temperature approach in of 2 °C	multi stream heat exchangers
Optimization Variables	Range	Step size	Optimization Variables	Range	Step size
 High pre. (P_{S101}) Low pre. (P_{S105}) 1st column inlet temp. (T_{S102}) 1st distillation column reflux ratio (RF₁) 1st distillation column reboiler temp. (RT₁) 2nd distillation column reflux ratio (RF₂) 2nd distillation column reboiler temp. (RT₂) 	46-55 bar 30-45 bar - 60 10 °C 1.5-5 10-15 °C 1.5-5 3-6 °C	0.5 bar 0.5 bar 2 °C 0.1 0.1 °C 0.1 0.1 °C	N_2 flow rate (M_{S201}) Low pre. (P_{S201}) High pre. (P_{S202}) Stage temp. (T_{S203})	3000–8000 kmol/h 1–5 bar 40–70 bar – 50– – 10 °C	100 kmol/h 0.5 bar 1 bar 2 °C

net electrical work that is used in the refrigeration cycle. Initially, the absorber column is optimized in such a way that the standard LBM specifications are satisfied considering the minimum work for biogas compression. In the second step, the heating duty of the reboiler of the stripper column is minimized. Finally, the liquefaction process is optimized in order to achieve minimum electrical work. The optimization problem for case 2, corresponding to Fig. 2, is given in Table 4.

3.3. Energy analysis

Calculations regarding energy requirements for the dehydration units consider the heat duties in the reboiler for TEG regeneration. The energy demand for the dehydration step is estimated in accordance with the methodology proposed by Kinigoma and Ani [39]. It is assumed that the hydration unit is able to dewater the stream completely. Moreover, heat loss from the dehydration unit is considered negligible. The lean TEG flow rate ($\dot{m}_{\rm lean TEG}$) in the dehydration unit is given as

$$\dot{m}_{\text{lean TEG}} = C_{\text{lean TEG}} \cdot \dot{V}_{\text{TEG}},\tag{1}$$

where $C_{\text{lean TEG}}$ is the concentration of lean TEG and \dot{V}_{TEG} is volumetric TEG circulation rate. The volumetric TEG circulation rate is calculated considering a TEG circulation ratio (CR_{TEG}) of 0.035 $m_{\text{TEG}}^3/kg_{\text{H2O}}$ [38]:

$$\dot{V}_{\rm TEG} = C R_{\rm TEG} \cdot \dot{m}_{\rm w} \tag{2}$$

Here, $\dot{m}_{\rm w}$ indicates the amount of water that is removed in the dehydration unit. The total heat rate requirement ($\dot{Q}_{\rm dh}$) (kJ/h) for the dehydration unit consists of the sensible heat rate for TEG ($\dot{Q}_{\rm s}$), the vaporization heat rate for water removal ($\dot{Q}_{\rm v}$) and the heat rate for the reflux flow stream ($\dot{Q}_{\rm r}$):

$$\dot{Q}_{\rm dh} = \dot{Q}_{\rm s} + \dot{Q}_{\rm v} + \dot{Q}_{\rm r}.$$
 (3)

Considering a reflux ratio (*R*) of 0.25, a TEG regeneration temperature of 200 °C and constant heat capacity (c_p) of 3.014 kJ/kg °C, given by Kinigoma and Ani [39], the heat requirement in the dehydration unit can be calculated by the following equations:

$$\dot{Q}_{\rm s} = \dot{m}_{\rm lean \ TEG} \cdot c_{\rm p} \cdot \Delta T \tag{4}$$

$$\dot{Q}_{\rm v} = 2.023 \cdot (\dot{m}_{\rm w} \cdot \dot{V}_{\rm gas \ flow}) \tag{5}$$

$$\dot{Q}_{\rm r} = R \cdot \dot{Q}_{\rm v} \tag{6}$$

Here, $\dot{V}_{gas \text{ flow}}$ (Nm³/h) is the volumetric gas flow rate entering the dehydration unit. The temperature differences (ΔT) for DH1 and DH2 corresponding to the model in Fig. 2 are defined as the difference between the TEG regeneration temperature and the temperature of the top

stream of the stripper and the absorber columns, respectively.

The thermodynamic performance of the proposed configurations in Section 2 are evaluated by means of energy. The overall energy efficiency is defined as the ratio of all useful energy to all required energy to produce the LBM [36]:

$$\eta = \frac{\dot{m}_{\text{LBM}} \cdot LHV_{\text{LBM}} + \sum \dot{W}_{\text{produced}} + \sum \dot{Q}_{\text{produced}}}{\dot{m}_{\text{rawbiogas}} \cdot LHV_{\text{rawbiogas}} + \sum \dot{W}_{\text{required}} + \sum \dot{Q}_{\text{required}}}.$$
(7)

Here, $\dot{m}_{\rm LBM}$ and $\dot{m}_{\rm raw biogas}$ are the mass flow rates of LBM and raw biogas, respectively. \dot{W} and \dot{Q} represent the work and heat rate produced or consumed in the plant. In this study, LCO₂ is considered a valuable byproduct from the plant that can be used in other applications. The lower heating value (*LHV*) of the streams, work and heat rates are obtained from simulation in Aspen HYSYS^{*}.

Besides the overall energy efficiency, for the sake of enabling of comparison different energy forms, the amount of methane in the raw biogas that can be utilized as LBM is interpreted as an energy indicator in accordance with the net equivalent methane method proposed by Pellegrini et al. [25]. In this method, the work and the heat requirements are converted into corresponding amounts of methane required to provide such energy requirements through conventional engineering processes. Considering energy efficiencies of engineering processes given by Pellegrini et al. [25], it is assumed that the work is generated from a combined cycle power plant with energy efficiency of $\eta_{cc} = 0.55$ when the power plant is fueled by the methane with a lower heating value of 50 MJ/kg [25]. However, the assumed energy efficiency of the power plant would in reality be lower on a typical LBM scale in range of 10–15 MW. The equivalent methane requirement for work (\dot{m}_{work}) can be expressed as

$$\dot{m}_{\rm work} = \frac{\dot{W}_{\rm net}}{\eta_{\rm cc} \cdot LHV_{\rm methane}},\tag{8}$$

where $\dot{W}_{\rm net}$ is the net work required for LBM production. In addition, it is assumed that the heat delivery at high temperature level in the reboiler of the stripper is supplied through a low-pressure steam generated by a methane-fired boiler with an energy efficiency of $\eta_{\rm b} = 0.80$ [25]. Hence, the equivalent methane requirement of the methane-fired boiler ($\dot{m}_{\rm heat}$) is given as

$$\dot{m}_{\rm heat} = \frac{Q_{\rm reb}}{\eta_{\rm b} \cdot LHV_{\rm methane}}.$$
(9)

Here, \dot{Q}_{reb} is the amount of heat required in the reboilers at high temperatures. Calculation of the equivalent methane for the required work and heat provides a practical measure to compare the proposed

Absorber (step 1)			Stripper (step 2)			Liquefaction (step 3)		
Objective Constraints	min {W _{biogas} compressi - CO ₂ content in Li - No H ₂ S content ii	_{on} } BM < 50 ppm n LBM	Objective Constraints	min {heating duty in Minimum temperatu heat exchanger (HX1	1 reboiler} re approach in intermediate) of 2°C	Objective Constraints	min {W _{N2} compression – W _{E1} · Minimum temperature appr exchangers of 2 °C	– W _{E2} } roach in multi stream heat
Optimization Variables	Range	Step size	Optimization Variables	Range	Step size	Optimization Variables	Range	Step size
Feed gas pre. (P _{S101})	35-55 bar	1 bar	Stripper pre. (P _{S106})	1–5 bar	0.5 bar	N_2 flow rate (M_{S201})	2000-7000 kmol/h	100 kmol/h
lean amine flow rate (L _{\$102})	4000–9000 kmol/h	500 kmol/h	Number of tray in stripper	15–25	1	Low pre. (P _{S201})	1–5 bar	0.5 bar
MDEA concentration	15-55 wt%	5 wt%	Feed tray	8-13	1	High pre. (P _{S202})	40–70 bar	2 bar
Number of tray in absorber column	15-30	1	Stripper reflux ratio (RF ₁)	1.5–5	0.5	Stage temp. (T _{S203})	-60 to -20°C	1 °C
			Stripper condenser temp. (CT ₁)	30-50 °C	5 °C	Intermediate temp. (T _{S115})	−60 to −20 °C	5 °C

Table

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configurations. Methane utilization (*MU*) indicates the amount of methane in the raw biogas ($\dot{m}_{CH4, raw biogas}$) that can be converted to LBM when all energy interactions involved in the process is treated as the equivalent methane:

$$MU = \left(1 - \frac{\dot{m}_{\text{work}} + \dot{m}_{\text{heat}} + \dot{m}_{\text{loss}}}{\dot{m}_{\text{CH4,rawbiogas}}}\right).$$
 (10)

Here, $\dot{m}_{\rm lossloss}$ denotes the amount of methane lost with the other streams of the LBM production plant. Results from the energy analysis are presented in Section 4.

3.4. Sensitivity analysis

Once the processes were optimized for a biogas mixture of 60 mol% CH_4 , 39.9 mol% CO_2 and 0.1 mol% H_2S , the optimum processes were used to perform sensitivity studies. In this study, the influence of the composition of the raw biogas on the specific energy use is considered for different CH_4 contents ranging from 40 mol% to 70 mol% while the H_2S concentration varies between 0.01 mol% and 1.0 mol%.

4. Results and discussion

The pressure, temperature, molar flow rates, and gas composition of streams corresponding to the optimized configurations of case 1 and case 2 are presented in Tables 5 and 6, respectively. The strict specification of producing biomethane with CO_2 content below 50 ppm results in the optimum value of 47 bar for the operating pressure of the absorber column in case 2. However, the optimized pressure value of the high-pressure distillation column in the case 1 is lower (i.e. 50.5 bar). This means the required work for biogas compression is greater in case 1. Moreover, results from Tables 5 and 6 illustrate that the molar flow rate of nitrogen in the optimized liquefaction process of case 2 is half of case 1, while the high pressure of the liquefaction process in both configurations equals 70 bar.

Distribution of the energy use in different processes for the two optimized configurations is given in Table 7. The total energy demand for case 1 includes electrical work used in compressors and pumps, and the refrigeration cycle. For case 1, the refrigeration cycle consumes more than 80% of the total required work of the plant because cooling duties in the condensers of the distillation columns are provided at different temperature levels. In addition, due to a higher refrigerant flow rate, the work requirement of the nitrogen compression unit is higher in case 1 than in case 2. In case 1, CO₂ compression requires a minor amount of the total work (i.e. less than 0.1%) since the

Table 5	
The optimized thermodynamic data of case 1 corresponding Fig.	1.

Stream	Molar flow	Temp. (°C)	Pre. (bar)		Composition (
	(KIIIOI/II)			CH_4	CO_2	H_2S	N_2
Raw biogas	1000.0	35.0	1.0	60.00	59.90	0.10	-
S101	1000.0	35.0	50.5	60.00	59.90	0.10	-
S102	1000.0	-10.0	50.5	60.00	59.90	0.10	-
S103	659.5	-70.3	50.5	90.79	9.19	0.02	-
S104	340.5	13.8	50.5	0.36	99.37	0.27	-
S105	659.5	-78.5	39.5	90.79	9.19	0.02	-
S106	598.6	-87.7	39.5	99.99	43 ppm	-	-
S107	60.9	4.1	39.5	0.25	99.62	0.13	-
S108	60.9	5.6	50.5	0.25	99.62	0.13	-
S109	598.6	-160.9	39.5	99.99	43 ppm	-	-
S201	6400.0	32.7	2.5	-	-	-	100
S202	6400.0	35.0	70.0	-	-	-	100
S203	6400.0	-36.0	70.0	-	-	-	100
S204	6400.0	-162.9	2.5	-	-	-	100
S205	6400.0	-136.2	2.5	-	-	-	100
LBM	598.6	-161.4	1.0	99.99	43 ppm	-	-
LCO_2	401.4	12.7	50.5	0.34	99.41	0.25	-

Table 6The optimized thermodynamic data of case 2 corresponding Fig. 2.

Stream	Molar flow (kmol/h)	Temp. (°C)	Pre. (bar)					Composition (mol%)		
				CH ₄	CO_2	H_2S	H ₂ O	MDEA	N_2	
Raw biogas	1000.0	35.0	1.0	60.00	59.90	0.10	-	-	-	
S101	1000.0	35.0	47.0	60.00	59.90	0.10	-	-	-	
S102	8000.0	45.0	47.0	-	0.03	4 ppm	88.96	11.01	-	
S103	594.5	45.0	47.0	99.71	47 ppm	-	0.29	-	-	
S104	8406.0	70.9	47.0	0.09	4.77	0.01	84.65	10.48	-	
S105	8406.0	69.2	2.5	0.09	4.77	0.01	84.65	10.48	-	
S106	8406.0	102.4	2.5	0.09	4.77	0.01	84.65	10.48	-	
S107	416.6	35.0	2.5	1.74	95.71	0.24	2.31	-	-	
S108	7989.0	130.0	2.5	-	0.03	4 ppm	88.94	11.03	-	
S109	7989.0	130.8	47.0	-	0.03	4 ppm	88.94	11.03	-	
S110	7989.0	71.2	47.0	-	0.03	4 ppm	88.94	11.03	-	
S111	8000.0	71.2	47.0	-	0.03	4 ppm	88.96	11.01	-	
S112	407.0	35.0	2.5	1.79	97.97	0.24	-	-	-	
S113	407.0	35.0	47.0	1.79	97.97	0.24	-	-	-	
S114	592.8	45.0	47.0	99.99	47 ppm	-	-	-	-	
S115	592.8	-40.0	47.0	99.99	47 ppm	-	-	-	-	
S116	592.8	-160.8	47.0	99.99	47 ppm	-	-	-	-	
S201	3200.0	34.1	1.5	-	-	-	-	-	100	
S202	3200.0	35.0	70.0	-	-	-	-	-	100	
S203	3200.0	-18.0	70.0	-	-	-	-	-	100	
S204	3200.0	-163.2	1.5	-	-	-	-	-	100	
S205	3200.0	-92.2	1.5	-	-	-	-	-	100	
LBM	592.8	-191.4	1.0	99.99	47 ppm	-	-	-	-	
LCO_2	407.0	10.9	50.5	1.79	97.97	0.24	-	-	-	

compression takes place in liquid form through pumps.

The amount of required work in case 2 is approximately 27% less than that in case 1, but the need of additional heat at elevated temperature levels increases the energy use in case 2. The refrigeration cycle in case 2 consumes 64.3% of the total work followed by biogas compression, CO_2 compression and MDEA compression with 25.5%, 7.7%, and 2.5%, respectively. Moreover, a large amount of heat is required to regenerate MDEA in the stripper column in case 2 (i.e. 97.3% of the total heat demand) and 2.7% of the total heat requirement is used in the dehydration units to regenerate TEG.

Results from Table 7 demonstrate that the work requirement for the refrigeration cycle in case 2 is approximately 42% lower than that in case 1. This is mainly because of selecting the single expander refrigeration cycle. Therefore, modifications regarding the type of refrigeration cycle such as employing cascade liquefaction processes or mixed refrigerant processes, which is appropriate for delivering cooling duties at different temperature levels in the condensers of the distillation columns, can benefit the energy use of the refrigeration cycle.

The specific energy use for the two optimized cases is indicated in Fig. 3. The results for models considering necessary units of operation for LBM production illustrate a specific energy use of 2.07 kWh/kg of LBM for case 1. Nevertheless, the specific energy requirement for case 2 consists of work with 1.54 kWh/kg of LBM and heat with 1.81 kWh/kg of LBM for a mixture of raw biogas with 60 mol% methane, 59.9 mol% CO_2 and 0.1 mol% H₂S.

The specific energy use as a function of CH₄ and H₂S concentration

in the raw biogas for case 1 and case 2 is given in Figs. 4 and 5, respectively. The higher the methane content in the raw biogas, the lower the specific energy requirement. Fig. 4 illustrates that the energy use per kg of produced LBM is reduced from 3.08 to 1.93 kWh/kg of LBM when the methane content in the raw biogas is increased from 40 mol% to 70 mol%. However, an increase in the H₂S concentration from 0.01 mol% to 1.0 mol% does not influence the specific energy use. The total specific energy use for case 2 presents the same trend as in case 1, where the specific energy use is reduced from 5.97 to 2.58 kWh/kg LBM by increasing the methane content from 40 mol% to 70 mol% (see Fig. 5).

The overall efficiency for the two cases is illustrated in Fig. 6. For case 1, the overall energy efficiency is 87.2% whereas it reduces to 80.1% for case 2. Moreover, the results indicate that the methane loss in case 1 is 80% less than that in case 2 (see Fig. 6).

Results from the net equivalent methane method is given in Fig. 7. For case 1, 72.7% of the methane available in the raw biogas for case 1 can be converted into LBM after using the required amount of methane for process operations, whereas in case 2, 62.8% of the methane available in the raw biogas can be utilized as LBM. In other words, the methane utilization of the cryogenic upgrading scheme is approximately 14% greater than that in the chemical absorption upgrading scheme.

Performing a detailed energy analysis of the two studied cases implies that a synergetic approach of upgrading and liquefaction through employing cryogenic distillation columns not only improves the energy

Table 7	
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Energy	distribution	for	different	processes	in	case	1	and	case	2
. 07				F						

Cryogenic u	pgrading scheme ((Case 1)		Chemical abs	Chemical absorption upgrading scheme (Case 2)			
	MW		%		MW		%	
Work	19.9	Biogas compression Refrigeration cycle	19.2 80.8	Work	14.6	Biogas compression Refrigeration cycle CO ₂ compression	25.5 64.3 7.7	
		CO ₂ compression	< 0.1	Heat	17.2	MDEA compression MDEA regeneration Dehydration units	2.5 97.3 2.7	



Fig. 3. Specific energy use for case 1 and case 2.



Fig. 4. The specific energy use as a function of CH_4 and H_2S concentration in raw biogas or case 1.



Fig. 5. The specific energy use as a function of CH_4 and H_2S concentration in raw biogas for case 2.

efficiency of the LBM production plant, but also converts a higher amount of the methane available in the raw biogas into LBM. However, in order to provide a better estimation of the performance of the two proposed cases, implementation of novel combined heat and power plants (CHP) with back pressure steam turbines should be considered since CHP plants can provide both heat and work with higher energy efficiencies. Moreover, the use of back pressure steam turbines can result in vacuum operation condition in the stripper column, which may lead to reduced heating requirements in the reboiler.

In Fig. 7, a comparison of the results in this study with results provided by Pellegrini et al. [25] (where the power consumption of the liquefaction process is estimated based on the temperature levels of the cooling requirements and a second law efficiency of 60%) illustrates that considering a complete model with refrigeration cycle and dehydration units in the two proposed configurations reduces the methane utilization by approximately 15% and 12% for case 1 and case 2, respectively. This is primarily due to the fact that the most energy intensive process in the LBM production is the liquefaction process. Consequently, simulation of the refrigeration cycles is required to provide a better understanding of the potential improvement of different LBM production configurations.

5. Conclusions

Complete models of two different configurations to produce LBM from raw biogas have been considered and optimized using Aspen HYSYS^{*} V9.0. In case 1, a cryogenic biogas upgrading method by means of two distillation columns at different pressure is integrated with liquefaction, while case 2 investigates a conventional chemical absorption upgrading using MDEA followed by a refrigeration cycle.

The raw biogas comprises a mixture of 60 mol% CH₄, 59.9 mol% CO₂ and 0.1 mol% H₂S. Important design variables of models were optimized using an exhaustive search method in order to minimize the energy use of each model.

Energy analysis was performed by considering the overall energy efficiency of the LBM production plant and the equivalent methane method. For case 1, the required specific work is 2.07 kWh/kg LBM while this value for case 2 is 1.54 kWh/kg LBM. However, the additional specific heat of 1.81 kWh/kg LBM is required for case 2 in order to regenerate MDEA and TEG in the upgrading step and dehydration units, respectively.

The overall energy efficiency of case 1 and case 2 is 87.2% and



Fig. 6. The overall energy efficiency and the methane loss for case 1 and case 2.



Fig. 7. Methane utilization in case 1 and case 2.

80.1%, respectively. In addition, case 1 is able to utilize 72.7% of the available methane in the raw biogas as LBM whereas this value is 62.8% in case 2. The energy analysis shows that a cryogenic upgrading scheme converts approximately 14% more of the available methane in the raw biogas into the LBM compared with a chemical absorption upgrading scheme. Results from the energy analysis demonstrates that a cryogenic upgrading scheme is favorable in terms of the overall efficiency of the LBM production plant and methane utilization.

Furthermore, results from energy distribution reveal that the main share of required work in the LBM production is used in liquefaction, approximately 81% and 64% in case 1 and case 2, respectively. Therefore, considering an appropriate type of liquefaction process with respect to the biogas upgrading method is worth being studied further. Meanwhile, heat integration potential from the LBM production plants will also be investigated in further work. For this future work, a more comprehensive optimization method will be applied.

Acknowledgements

Financial support from the Norwegian University of Science and

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ENERSENSE is greatly acknowledged.

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