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TECHNO-ECONOMIC ANALYSIS OF BIOMETHANE PRODUCTION WITH NOVEL UPGRADING TECHNOLOGY

Report from a project within the collaborative research program *Renewable transportation fuels and systems*

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Authors: Xiaoyan Ji, Yujiao Xie, Chunyan Ma (Bio4Energy/Luleå University of Technology), Johanna Björkmalm, Karin Willquist, Johan Yngvesson (SP Technical Research Institute of Sweden) and Ola Wallberg (Faculty of Engineering, Lund University)

THE SWEDISH KNOWLEDGE CENTRE
FOR RENEWABLE TRANSPORTATION FUELS

PREFACE

This project is financed and carried out within the f3 and Swedish Energy Agency collaborative research program *Renewable transportation fuels and systems* (Förnybara drivmedel och system).

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- Carries through system oriented research related to the entire renewable fuels value chain
- Acts as national platform stimulating interaction nationally and internationally.

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NOMENCLATURE

AD	anaerobic digestion
ILs	ionic liquids
ConvIL1	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N])
ConvIL2	1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6])
ConvIL3	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N])
NovIL1	50wt% choline chloride/urea (ChCl/Urea) + 50wt% water
NovIL2	90wt% 1-allyl-3-methyl imidazole formate ([Amim][HCOO]) + 10wt% water
TAC	total annual cost
ACC	annual capital investment cost
OMC	operation and maintenance cost
EC	equipment cost
TCC	total capital investment cost

EXECUTIVE SUMMARY

The use of upgraded biogas (biomethane) as vehicle fuel has been considered as one of the most efficient means of utilizing renewable fuels to reduce greenhouse-gas emissions from the transportation sector. Although several technologies have been developed and commercialized to upgrade biogas, they are energy intensive and usually require large-scale operations. It thus calls for exploring energy- and cost-effective technologies for biogas upgrading to improve the overall economics of biogas processes.

Ionic liquids (ILs) have shown great potential to be used as liquid absorbents for CO_2 removal from different gas streams (e.g. biogas upgrading) because of high CO_2 solubility (i.e. high absorption capacity) and low energy requirement for regeneration (i.e. low energy usage and low cost). A lot of ILs have been synthesized, and thermo-physical properties of ILs have been measured extensively. However, the performance evaluation of different ILs on biogas upgrading has not been extensively studied. Meanwhile, biogas upgrading is one sub-process of biomethane production. The operational conditions (temperature, pressure, CH_4 content, etc.) of both upstream and downstream processes will affect the performance of biogas upgrading. The implementation of new biogas upgrading technology will also affect the overall economics and energy usage. How to implement the new IL-based biogas upgrading technology and then evaluate the performance of the overall process is important for further industrial studies but has not yet been investigated. The investment cost is crucial for technology implementation, but for the assessment to have substance to the biogas sector, academic techno-economical studies need to be validated in respect to measured data of commercial biogas production and upgrading.

In this cooperative project, both conventional and novel ILs were chosen as liquid solvents for biogas upgrading in order to investigate how the properties of ILs affected the process performance in respect to commercial co-digestion facilities in Sweden and Norway. To achieve this, three conventional ILs (ConvIL1, ConvIL2, ConvIL3) and two novel ILs (NovIL1, NovIL2) were chosen. Their properties and the gas solubilities in these ILs were represented with the models embedded in the simulation software Aspen Plus. After the implementation of the model parameters, the process simulation of biogas upgrading with these ILs was performed in Aspen Plus. The NovIL2 scrubbing was further simulated with input data from Swedish and Norwegian industrial biogas processes using different substrates. An economic evaluation was made for the NovIL2 upgrading process and was compared to the industrial data from upgrading plants and the data from literatures.

For the three studied conventional ILs, the investigation shows that the amount of recirculated solvents and the total energy usage for upgrading process using ILs follow: ConvIL1 < ConvIL2 < ConvIL3, i.e. the performance of ConvIL1 is the best among these three ILs. The process with ConvIL1 was then chosen as an example to perform the sensitivity analysis. The results show that the pressure drop in the absorber increases with increasing density and viscosity of solvent. The absorber diameter increases with increasing viscosity but changes slightly with increasing density. The CH_4 yield and CO_2 removal efficiency increase with increasing pressure in the absorber and the flash tank and decrease with increasing absorber temperature. The energy usage increases with increasing pressure and temperature in the absorber and decreases with increasing pressure in the flash tank.

The performance of the biogas upgrading technology with the ILs (ConvIL1, NovIL1, NovIL2) was further compared with water scrubbing. The comparison indicates that the IL technology is promising in respect to the amount of recirculated solvent and the total energy usage for the upgrading process, especially NovIL1 and NovIL2. The simulated results of energy efficiency and operational cost correspond well with the industrial data, showing the applicability of the model to simulate upgrading processes. The model shows that the greatest benefit of using IL technology is energy saving with a 35% saving in electricity, while the total capital cost (*TCC*) and the operation and maintenance cost (*OMC*) for the NovIL2 upgrading decrease by 7% and 10%, respectively, compared to water scrubbing. In the situation where electricity price increases, the IL technology can be an interesting alternative to conventional water scrubbing technology. This is especially relevant to the anerobic digestion raw biogas upgrading since many plants are currently struggling with profitability.

SAMMANFATTNING

Att uppgradera biogas till fordonsgas ses som ett av de mest effektiva sätten att använda förnybara bränslen för att minska utsläppen av växthusgaser i transportsektorn. Det finns ett flertal olika kommersiella uppgraderingstekniker, dock är de energiintensiva och kräver ofta storskalig implementering för att bli kostnadseffektiva. Det finns därmed ett incitament för att utveckla mer energi- och kostnadseffektiva tekniker för biogasuppgradering för att förbättra ekonomin i processen som helhet.

Joniska vätskor har visat sig ha stor potential som absorbent för att ta bort koldioxid i olika gasströmmar, t.ex. biogas. Det beror på att dessa vätskor har hög CO_2-löslighet och låg energianvändning för regenerering av vätskan. Många olika typer av joniska vätskor har framställts och deras termofysikaliska egenskaper har undersökts. Däremot saknas det en fullständig utvärdering av olika joniska vätskor för biogasuppgradering när det gäller energi och kostnader. En sådan teknoekonomisk utvärdering som också ställs i relation till data från kommersiella anläggningar är av vikt för framtida industriell applikation.

I detta projekt har både konventionella och nya joniska vätskor utvärderats för att se hur deras egenskaper påverkar processen i stort och jämförts med data från industriella biogas- och uppgraderingsanläggningar i Sverige och Norge. Tre konventionella joniska vätskor, (ConvIL1, ConvIL2, ConvIL3) samt två nya typer av joniska vätskor (NovIL1, NovIL2) har studerats. Deras egenskaper implementerades i simuleringsprogrammet Aspen Plus och en simuleringsmodell för biogasuppgradering med joniska vätskor sattes upp. Uppgradering med NovIL2 simulerades med startdata från svenska och norska industriella biogasprocesser. En ekonomisk utvärdering av uppgradering med NovIL2 genomfördes och jämfördes med industriell data från uppgraderingsanläggningar samt med data från litteratur.

För de tre konventionella joniska vätskorna värderades ConvIL1 bättre än ConvIL2 som är bättre än ConvIL3 avseende mängd lösning som behöver recirkuleras och den totala energianvändningen.

Resultaten från modellsimuleringarna av uppgradering med olika joniska vätskor ConvIL1, NovIL1 och NovIL2 jämfördes med vattenskrubberteknik. Simuleringen visar att joniska vätskor potentiellt kan vara en lovande teknik för uppgradering av biogas, speciellt när det kommer till energianvändning och mängd vätska som kan recirkuleras, detta gäller framförallt NovIL2 och NovIL1. Modellen visar att den största behållningen av att använda joniska vätskor ligger i energibesparingar med potentiellt 35% energibesparing medan den totala kapitalkostnaden och drift- och underhållskostnaden potentiellt kan minska med 7% respektive 10% jämfört med vattenskrubberteknik. Joniska vätskor kan därmed vara ett lovande alternativ till den mer konventionella vattenskrubbertekniken, vilket är av vikt då många biogasanläggningar idag kämpar med låg lönsamhet.

CONTENTS

1 INTRODUCTION

Renewable energy strategies need to be developed to secure a sustainable long-term energy supply and mitigate greenhouse-gas emissions. This is especially important in the transportation sector as it is a main fossil-energy consumer and CO_2 emitter in Sweden. The use of upgraded biogas (biomethane) as vehicle fuel is considered as one of the most efficient means of utilizing renewable fuels to reduce greenhouse-gas emissions from the transportation sector.

Biogas is a promising renewable energy alternative due to the flexibility of anaerobic digestion (AD) where a spectrum of organic substrates, such as manure, sewage sludge, energy crops, the organic fractions of household, and industrial waste can be used [1-2]. In Sweden, 1.4 TWh biogas was produced from 230 production units in 2010 and the theoretical potential for Swedish biogas will be 15 TWh/y, which is around ten times more than the current production [3]. The biogas production in the European Union has steadily increased over the past years [4].

Biogas consists mainly of methane (CH_4) and carbon dioxide (CO_2), with small amounts of hydrogen sulfide (H_2S), water (H_2O), hydrogen (H_2), nitrogen (N_2) and oxygen (O_2). The methane content in AD-produced biogas ranges between 50 and 70% [5]. To be used as vehicle fuel, CO_2 needs to be removed to a level of $CH_4 > 97\%$, according to the Swedish regulations, SS 155438:2015 [6], and this is termed “upgrading”. The main upgrading technology used in Sweden is water scrubbing [7]. It produces a large amount of wastewater, requires a high capital investment and energy usage but still has a fairly low CO_2 capture efficiency. The aqueous amine-based technology uses up to 30% of the energy of the gas and is associated with volatility, amine degradation and corrosion. Membrane processes are promising, but the selectivity and sometimes even productivity are lost in the presence of CO_2. Other methods (pressure swing adsorption, cryogenic separation, etc.) are also energy intensive and usually require large-scale operations [7]. It thus calls for exploring energy- and cost-effective technologies for biogas upgrading (i.e. CO_2 separation or removal from raw biogas) to significantly improve the overall economics of biogas processes.

Ionic liquids (ILs) are molten salts that do not evaporate and are widely anticipated as potentially environmentally benign solvents. ILs have shown great potential to be used as liquid absorbents for CO_2 removal because of high CO_2 solubility (i.e. high absorption capacity) and low energy requirement for regeneration (i.e. low energy usage and low cost). A lot of ILs have been synthesized, and thermo-physical properties of ILs have been measured extensively [8]. However, the performance evaluation of different ILs on biogas upgrading has not been well studied [9].

The biogas upgrading using ILs is a combination of absorption and solvent regeneration (desorption), and their operational conditions and IL properties will determine the energy usage and other costs. However, most of the available work is on the absorption part, i.e. the solubility of target gas in ILs and its selectivity as the main research focus [8]. Meanwhile, biogas upgrading is one subprocess of biomethane production. The operational conditions (temperature, pressure, CH_4 content, etc.) of both upstream and downstream processes will affect the performance of biogas upgrading. The implementation of new biogas upgrading technology will also affect the overall economics and energy usage. How to implement the new IL-based biogas upgrading technology and then evaluate the performance of the overall process is important for further industrial studies but has not yet been investigated. The investment cost is crucial for technology implementation, and a conceptual design via commercial software Aspen Plus can provide such information. However, for the assessment to have substance to the biogas sector, academic technoeconomical studies need to be validated in respect to the measured data of commercial biogas production and upgrading. However, the comparison of simulation results and data from commercial biogas upgrading facilities is to our knowledge lacking in the literature.

In this cooperative project, three conventional ILs (ConvIL1, ConvIL2, ConvIL3) and two novel ILs (NovIL1, NovIL2) were chosen as liquid solvents for biogas upgrading, and their performance was evaluated and compared by conducting process simulation via commercial software Aspen Plus with the consideration of commercial co-digestion facilities in Sweden and Norway. The measured data from Swedish and Norwegian industrial biogas processes using different substrates was used to validate the simulation results of water scrubbing, and then used as input data to simulate the NovIL2 scrubbing for further comparison. In addition, an economic evaluation was made for the NovIL2 upgrading process and compared to the industrial data from upgrading plants and the data from literatures.

2 PROCESS DESCRIPTION

To produce biomethane from various organic substrates, anaerobic digestion (AD) is one of the effective methods. There are a range of different substrates that can be utilized for biogas production, such as food waste from households and restaurants, waste and by-products from the food and feed industry, manure, energy crops, as well as by-products from ethanol production, i.e. ethanol stillage. Food waste itself can be an inhomogeneous substrate with great variations and, therefore, always requires pretreatment and homogenization to create a pumpable slurry with a dry matter content of 10-15%. Common substrates for Swedish and Norwegian co-digestion plants are food waste, waste and by-products from food and feed industry, and in some cases manure and energy crops.

The process can be illustrated as in Figure 1. The substrate is collected and pretreated to increase the process efficiency. The pretreated substrate is entered into the fermentation tank, and raw biogas is generated. The composition of the raw biogas with respect to CH_4 and the gas flow rate are dependent on the type and the amount of substrate as well as the configuration of the anaerobic digestion process, e.g. the retention time in the digester. The raw biogas is cleaned and purified, i.e. upgraded, to remove CO_2 and other impurities. The upgraded biogas with > 97% CH_4 is termed as biomethane, and it can be used as vehicle fuel or further converted to industrial chemicals. The digestate from the fermentation tank is entered to a storage tank for further treatment or utilization as fertilizer.

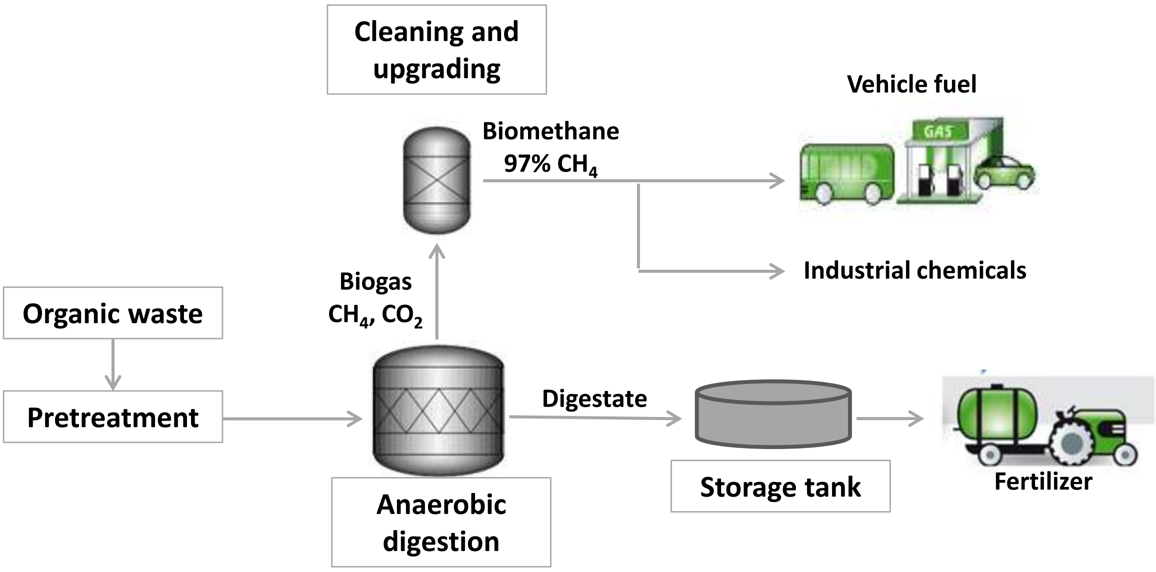

Figure 1. The schematic picture of biomethane production from organic waste.

The process of biogas upgrading with dry or aqueous ionic liquids (ILs) as well as water was simulated in Aspen Plus, and the schematic of the conceptual process is illustrated in Figure 2 and 3, including CO_2 absorption, flash (gas recirculation), and solvent regeneration.

(1) CO_2 absorption. The biogas is pressurized to 8 bar in the compressors and injected into the bottom of the absorber, and the solvent is sprayed from the top of the absorber. CH_4 is obtained on the top of the absorber.

(2) Flash (gas recirculation). The CO_2-enriched solvent enters the flash. The gas released from flash is recirculated to the second compressor and mixed with the raw biogas.

(3) Solvent regeneration. The CO_2-enriched solvent is sent to the desorber and regenerated by decreasing the pressure to 1 bar with an aeration of air using a blower (Figure 2). The solvent leaving from the bottom of the desorber is recirculated and mixed with make-up solvent. When the dry ILs were used as the solvent to remove CO_2, the desorber in Figure 2 is replaced by the flash tank, and the solvent is regenerated by decreasing the pressure due to the low vapor pressure of ILs. The process is illustrated in Figure 3.

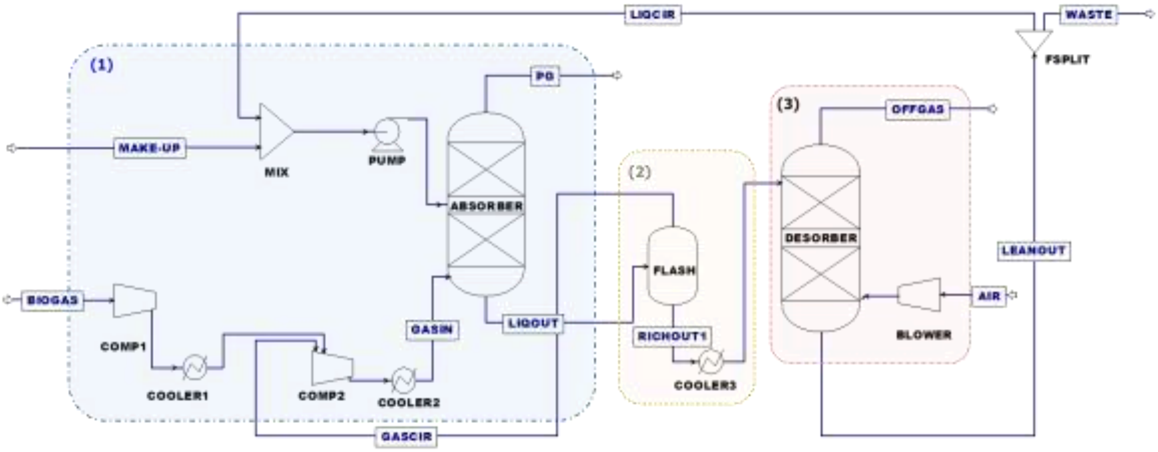

Figure 2. The schematic picture of biogas upgrading with aqueous ILs or water.

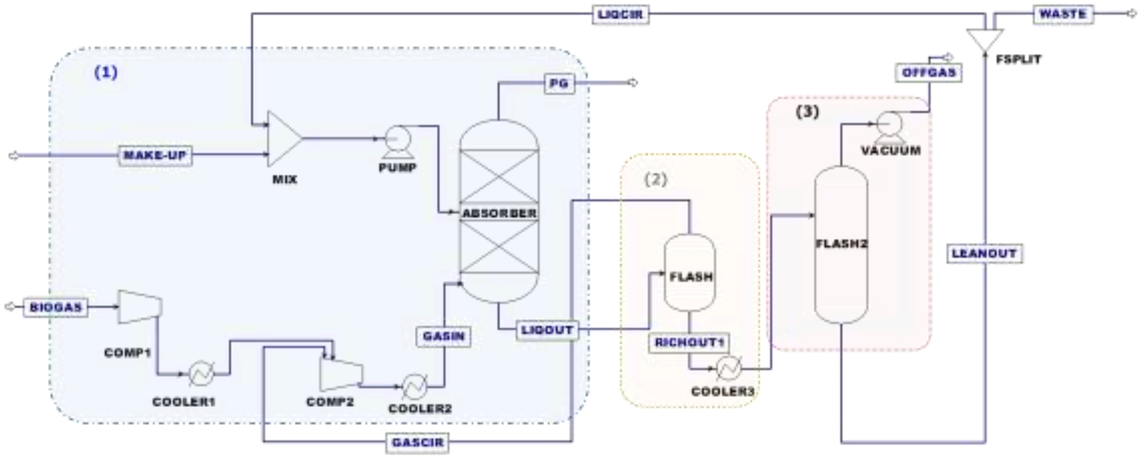

Figure 3. The schematic picture of biogas upgrading with dry ILs.

In the simulation, the biogas was assumed to be a mixture of 55% CH_4 and 45% CO_2. The simulation was based on the equilibrium approach. A 97% purity of CH_4 can be reached in the product gas (PG) by varying the amount of ILs. The CH_4 loss is related to many factors including the amount of ILs, the pressure of the absorber, and the pressure of the flash. It can be controlled to be lower than 1% by varying the pressure of the flash while the other operational parameters (e.g. the amount of ILs) are kept as constants. The process parameters used in the simulation are listed in Table 1.

Table 1. The parameters of biogas upgrading used in the process simulation.

Parameter	Units	Values
CH_4/CO_2	vol.%	55/45
P_{biogas}	bar	1
T_{biogas}	K	293
$P_{absorber}$ / $P_{desorber\ for\ water/aqueous\text{-}IL\ scrubbing}$	bar	8/1
$P_{absorber}$ / $P_{desorber\ for\ dry\ IL\ scrubbing}$	bar	8/0.1
$T_{absorber}$ / $T_{desorber}$	K	293/293
Plant capacity	Nm^3/h	224
$N_{stage\ of\ absorber}$		11
Purity of CH_4	%	97
CH_4 loss	%	<1

3 METHODOLOGY

3.1 MODELLING, PARAMETERIZING AND IMPLEMENTATION

To conduct process simulation, models with parameters are needed to describe the phase equilibria as well as critical and thermo-physical properties. For ionic liquids, the group contribution method was used to estimate the critical properties, while those for other components were taken from Aspen databank. The thermodynamic and transport properties such as density, viscosity, surface tension and heat capacity play a vital role in process simulation. The available experimental data of these properties was surveyed and evaluated. The consistent experimental data was then fitted to the empirical equations embedded in Aspen Plus. The Non-Random Two Liquids (NRTL)-Redlich–Kwong (RK) model was used in order to represent the gas solubility in dry and aqueous ILs as well as in H_2O. The details of the models and equations can be found in the Appendix.

3.2 DATA FROM INDUSTRIAL PLANTS

In order to evaluate the results from the upgrading model with ILs, operation and maintenance data was taken from six different co-digestion plants in Sweden and Norway, treating mainly food waste from households and restaurants as well as waste and by-products from various food industries. The data was collected on an annual basis through a survey within the scope of another ongoing project (project no 39183-1, financed by the Swedish Energy Agency). The collection included the data from the anaerobic digestion plant as well as that from the upgrading process.

The amount of treated substrate, the amount of raw gas produced, the methane content of the raw gas, the energy usage and the cost for the upgrading process were selected as important input data and/or benchmarking data for assessing the novel upgrading process with ILs. Based on the collected data, the energy usage as well as the operation and maintenance cost on the biogas upgrading process for each plant were calculated and compared to the corresponding figures obtained from the simulation of the upgrading process with ILs.

3.3 ECONOMIC EVALUATION

The cost of the process for biogas upgrading using ILs was estimated based on the following description. The total annual cost (*TAC*) includes the annual capital investment cost (*ACC*) and the operation and maintenance cost (*OMC*). The annual capital investment cost (*ACC*) was converted from the total capital investment cost (*TCC*) according to Eq. (1):

$$ACC = TCC \cdot \frac{i(1+i)^n}{(1+i)^n - 1} \tag{1}$$

where n and i are assumed to be 15 and 0.09, which refer to the economic lives of the equipment and the interest rate, respectively.

The total capital investment cost (*TCC*) can be estimated from the equipment cost (*EC*) as summarized in Table 2. The *EC* was estimated with the Guthrie's method [10]:

$$EC = PC \cdot (f_{mp} + f_m - 1) \tag{2}$$

where f_{mp} is the material and pressure correction factor, f_m is the module factor taking the size of the equipment into account, and *PC* is the bare purchased equipment cost.

The parameters f_{mp} and f_m depend on equipment. In this work, the values recommended by Scholz et al. [11] were used.

The purchased cost *PC* depends on equipment. For absorber, desorber and flash vessels, Eq. (3a) was used to estimate the *PC* from their height (*l*) and diameter (*d*). For compressors, pumps and heat exchangers, Eq. (3b) was used and the parameter *S* characterizing the equipment, i.e. the electric power, heat exchange area, was obtained through Aspen Plus simulation.

$$PC = C_0 \left(\frac{l}{l_0}\right)^{\alpha} \left(\frac{d}{d_0}\right)^{\beta} \tag{3a}$$

$$PC = C_0 \left(\frac{S}{S_0}\right)^{\alpha} \tag{3b}$$

where C_0 is the reference cost, and S_0, l_0 and d_0 are the reference size characteristic values for the equipment taken from Scholz et al. [11].

The operation and maintenance cost (*OMC*) consists of maintenance cost, operating supply cost, research and development (R&D) cost, utility costs (i.e. electricity, steam and cooling water, absorbent replacement cost). The method used by Scholz et al. [11] and Huang et al. [12] as shown in Table 2 was used to estimate this cost.

Table 2. General cost estimation for total capital cost and operating cost.

Total capital investment cost (*TCC*)		**Annual operation and maintenance cost (*OMC*)**	
Direct cost (*DC*)	% of *EC*	**Fixed charge (*FC*)**	
equipment (*EC*)	100	local taxes	1% of *FCI*
equipment installation	47	insurance	1% of *FCI*
instrumentation and control	36	total fixed charge (*TFC*)	
piping	68	**Direct production Cost (*DPC*)**	
electrical	11	maintenance (*M*)	3% of *FCI*
building and building services	18	operating labour (*OL*)*	
yard improvement	10	supervision (*S*)	15% of *OL*
service facilities	70	operating supplies	15% of *M*
total direct cost (*TDC*)	360	laboratory changes	15% of *OL*
Indirect cost (*IC*)	% of *EC*	plant overhead	15% of (*M*+*OL* +*S*)
engineering	33	electricity	
construction expenses	41	total direct production cost (*TDPC*)	
legal costs	4	**General expenses (*GE*)**	
contractor's fee	22	administrative cost	15% of *OL*
contingency	44	distribution and marketing	2% of OMC
total indirect cost (*TIC*)	144	R&D cost	2% of OMC
fixed capital invest (*FCI*)=*TDC* +*TIC*	504	total general expenses(*TGE*)	
working capital, 15% of *TCI*		solvent replacement cost	
IL cost		depreciation expense	
Total capital investment cost (*TCC*)= *TDC*+*TIC*+ working capital +IL cost		Operation and maintenance cost (*OMC*)=*TFC*+*TDPC*+*TGE*+ solvent replacement cost cost+ depreciation expense	

*1500 man-hours/year are assumed for the given plant capacity according to the results of the industrial plants.

In the cost estimation, an annual operation of 8600 h was used when calculating the operating cost. The price of IL was estimated to be 6600 $/t [12], the electricity price was set to be 0.10 $/kWh, and the hourly wage of operating labour (hourly personnel cost) was set to be 42 $/h corresponding to the results of the industrial plants.

4 PROJECT RESULTS

In this part, the research results are described briefly. The more specific description of the research results are illustrated in the article [13] which evaluates the conventional ionic liquid-based technology for biogas upgrading, conference proceeding [14] which evaluates the ionic-liquid based technology in integration with anaerobic digestion, and manuscript [15] which analyses the techno-economic possibilities with ionic-liquid based technology.

4.1 BIOGAS UPGRADING WITH CONVENTIONAL ILS

4.1.1 Properties of ILs and gas solubility in ILs

A literature survey was conducted in order to obtain the properties (e.g. density, viscosity, surface tension, heat capacity) of ILs and the solubility of CO_2 and other gases (e.g. CH_4) required for performing process simulation for biogas upgrading. The survey shows that the reported CH_4 solubility is only limited to three conventional ILs (ConvIL1, ConvIL2, ConvIL3) although a lot of ILs have been synthesized and the properties of ILs and the CO_2 solubility in ILs have been intensively studied.

The density, viscosity, surface tension and heat capacity of ConvIL1, ConvIL2 and ConvIL3 have been measured extensively at different temperatures and atmospheric pressure. The comparison of all the available experimental data from different sources shows that the density and viscosity from different sources are consistent with each other, while the experimental surface tension and heat capacity of ConvIL2 and ConvIL3 from different sources show considerable discrepancies. The disparities may be due to the impurity of ILs.

After the evaluation, the consistent data from different sources was fitted to the empirical equations in order to conduct process simulation. The comparison of the fitted results with the experimental data is illustrated in Figure 4, showing that the equations with the parameters can be used to reliably describe these properties.

The effects of alkyl chain length of cation and anion on the property of and the gas solubility in these three ILs were further investigated. It was found that the CO_2/CH_4 selectivity in ConvIL2 is high, but the viscosity and surface tension of ConvIL2 is also high. Compared to ConvIL2, the viscosity of ConvIL1 is low while the CO_2/CH_4 selectivity is also low. Principally, a promising solvent for biogas upgrading should have high CO_2 capacity/selectivity and low viscosity. Based on the comparison, it is unclear which IL is more promising. Therefore, it is important to conduct process simulation for comparing the performance of these ILs.

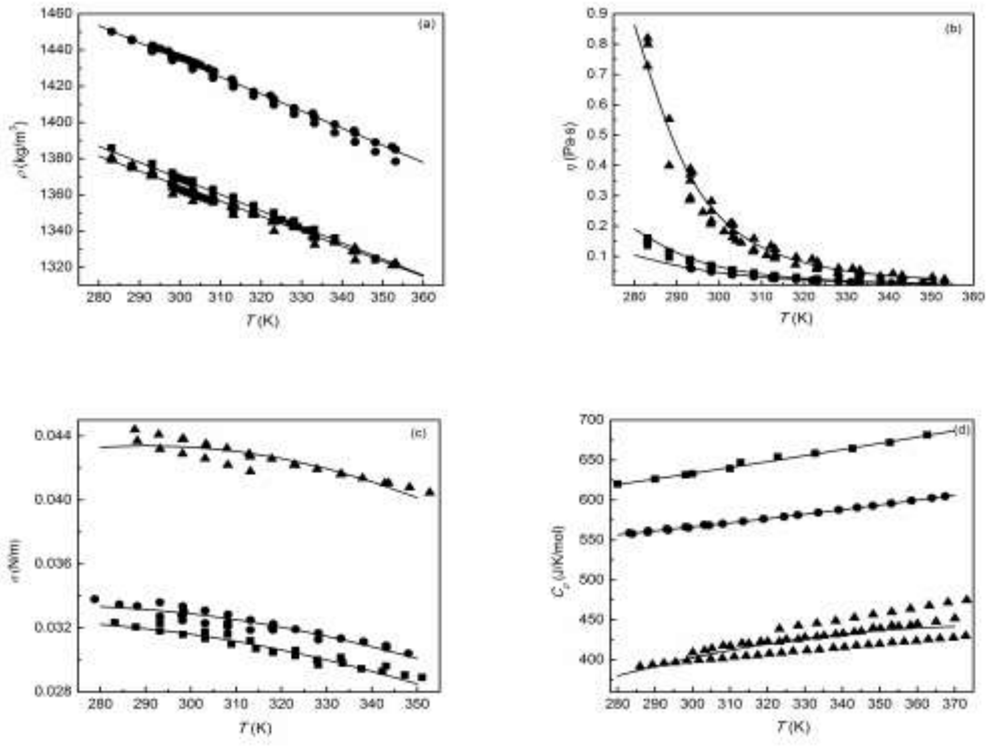

Figure 4. Temperature-dependent property of ●ConvIL1 ▲ConvIL2 ■ConvIL3 (a) density, (b) viscosity, (c) surface tension, (d) heat capacity. Symbols: experimental data. Curve: correlations.

4.1.2 Process simulation and performance evaluation

The conceptual processes for biogas upgrading with three conventional ILs were simulated with the parameters listed in Table 1 and the flowsheet described in Figure 3. The performances of these ILs were compared and evaluated. Meanwhile, sensitivity analysis was conducted to study how the properties of ILs affect the process performance.

The simulation results are listed in Table 3. The performance in respect to the possible amounts of recirculated solvents follows: ConvIL1 < ConvIL2 < ConvIL3. The gas loading in ILs is the key factor influencing the amount of solvent. The higher the CO_2 loading and the lower the CH_4 loading, the lower the amount of recirculated IL. Therefore, both CO_2 and CH_4 loadings are important for evaluating the performance of biogas-upgrading as the solubility of CH_4 in the ILs is not always extremely low compared to the CO_2 solubility.

Table 3. The simulation results for biogas upgrading with three conventional ILs

Unit	ConvIL1	ConvIL2	ConvIL3
Diameter of absorber, m	0.46	0.66	0.53
Make-up solvent, t/h	0.360	0.365	0.372
Recirculated solvent, t/h	23.64	23.97	24.45
Power, kW			
COMP 1	13.205	13.205	13.205
COMP 2	13.546	13.410	15.945
PUMP	6.884	9.444	7.744
VACUUM PUMP	7.447	8.453	8.454
total	41.082	44.512	45.348

The absorber diameters with different solvents follow the order of ConvIL1 < ConvIL3 < ConvIL2. The larger the absorber diameter, the higher the investment cost. The absorber diameter relates to the density and viscosity of solvents. At 293 K, the density of ConvIL1 is the highest while the viscosity is the lowest. The study reveals that the densities of the studied ILs only show a slightly difference comparing to the difference in their viscosities. Therefore, the viscosity of ILs is a key factor to determine the absorber diameter. Meanwhile, the total energy demands follow: ConvIL1 < ConvIL2 < ConvIL3. The power requirements of the pump are quite different because of the differences on the amounts of recirculated solvents. The vacuum pump power for ConvIL1 scrubbing is the lowest.

The process with ConvIL1 was chosen as a case study to further perform the sensitivity analysis on the pressure drop and absorber diameter. As shown in Figure 5, the pressure drop in the absorber increases with increasing density and viscosity of solvents. The absorber diameter increases with increasing viscosity but changes slightly with increasing density. The effects of pressure and temperature on the process efficiency were studied. The CH_4 yield and CO_2 removal efficiency increase with increasing pressure in the absorber and the flash tank and decrease with increasing absorber temperature. The CH_4 loss ratio shows opposite behaviours. The amount of recirculated solvent and the energy usage were calculated by fixing 97% purity of CH_4 in the product gas, and the energy usage increases with increasing pressure and temperature in the absorber and decreases with increasing pressure in the flash tank.

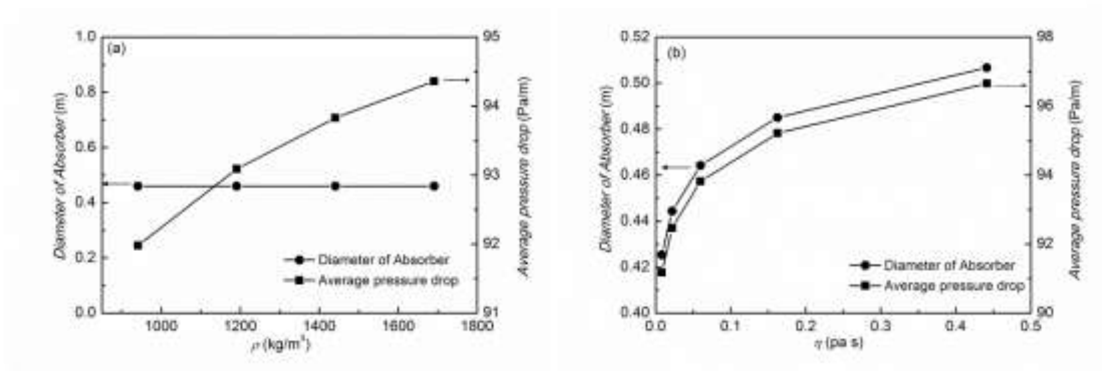

Figure 5. The effects of density (left) and viscosity (right) of IL on the diameter of absorber and pressure drop.

ConvIL1 scrubbing was compared with water scrubbing and NovIL1 scrubbing. It is found that NovIL1 scrubbing and ConvIL1 scrubbing show 29% and 11% reductions in energy usage, respectively, compared to water scrubbing. Therefore, the IL-based solvent can achieve energy-savings for biogas upgrading process, which implies that IL-technology is promising for biogas upgrading.

4.2 BIOMETHANE PRODUCTION

The biogas upgrading process was simulated with input data from industrial biogas plants. The performance of biogas upgrading with different solvents (ConvIL1, NovIL1, NovIL2 and water) was further compared.

4.2.1 Data from Swedish and Norwegian biogas plants

The main substrates used by the industrial plants are food waste from households and supermarkets as well as organic waste from food and feed industries. The sizes of the plants vary from 28 000 to 120 000 ton substrate treated per year, with a gas production ranging from about 2.2 to almost 10 million Nm^3/year (Table 4). Estimating 8 600 operating hours per year for the upgrading plant, these figures correspond to an upgrading capacity of about 250 up to 1150 Nm^3/hour. However, in reality, the upgrading capacity used at the plants ranges from 50 to 540 Nm^3/hour due to the fact that not all the produced biogas is upgraded, some is flared and some is used internally within the plant for heating. The amount of gas used for upgrading at plant C is not given. As can be expected, the larger the process, the higher the feed rate, also resulting in a higher raw gas flow rate. Plant A upgrades the biogas from the anaerobic digestion (AD) plant together with the biogas produced at the wastewater treatment plant, hence a larger number of raw gas flow rate for upgrading.

The data shows that the CH_4 content in the raw biogas from different plants varies between 61 and 69%. Compared to, for example, ethanol stillage which gives a ~50% CH_4 content in anaerobic digestion [16], the methane (CH_4) content in the biogas from the biogas plants treating food waste is higher due to the higher lipid content in the food waste compared to that in the ethanol stillage. All the industrial plants, except for plant F, use water scrubbing as upgrading technique, and all the plants reach a CH_4 content in the upgraded gas of 97% or higher.

Table 4. Industrial data from six selected representative industrial sites in Sweden and Norway*

AD process	Feed rate to digester	Raw gas flow rate	Raw gas flow rate for upgrading[1]	CH_4 content	CH_4 content in upgraded gas	Upgrading technology
	ton/year	*Nm^3/year*	*Nm^3/year*	$\%_{vol}$	$\%_{vol}$	
Co-digestion plant						
A	34 000	2 180 000	3 860 000[2]	63	97	Water scrubbing
B	28 000	2 460 000	440 000[3]	61	97	Water scrubbing
C	120 000	9 930 000	-	66	-	-
D	48 000	4 840 000	4 650 000	63	98	Water scrubbing
E	48 000	3 730 000	1 660 000	63	98.5	Water scrubbing
F	29 000	2 327 000	777 000	69	98	Membrane

[1]Some gas is flared or used internally at the AD plant for warming of buildings etc.

[2]In this case, gas is added from the wastewater treatment plant

[3]The upgrading plant is running at half speed

***treating food waste from households as well as organic waste from various food and feed industries as substrates; the data represents the year 2015 except for plant C which represents data from 2014**

4.2.2 Process evaluation and comparison

(a) Process simulation

The conceptual process as described in Figure 2 or Figure 3 for biogas upgrading using water, ConvIL1, NovIL1, and NovIL2 as solvents was simulated, respectively. The performance was evaluated according to flow balance and the amount of recirculated solvent. In the simulation, the parameters were set as those listed in Table 1.

The simulation results are listed in Table 5. In the off gas (OFFG), the difference in molar flow rates of CO_2 between the solvents was less than 10%. In the circulated gas (GASCIR), the CO_2 in the process with NovIL2 was three folds lower than the average of the tested solvents (2 kmol/h) as a result of the low CO_2 solubility in water. Correspondingly, in the recirculated liquid (LIQCIR), the CO_2 in the process with NovIL2 was four folds lower than the average (0.09 kmol/h). The lower CO_2 in the GASCIR resulted in a simulated lower amount of solvent which needed to be added in the makeup and recirculated solvent.

The higher flow rate of make-up solvent and recirculated solvent significantly affected the energy usage. The pump power for water scrubbing is quite large due to the large amount of recirculated water because of the low CO_2 solubility in water. However, there are no large disparities on the compression work. The vacuum pump was needed only for the process using ConvIL1 (Figure 3), resulting in a higher energy usage compared to NovIL1 and NovIL2. Compared to water scrubbing, the total energy usage for convIL1 scrubbing decreases with about 10%, while the energy usage for NovIL2 scrubbing decreases with around 30%. Therefore, in the next section, NovIL2 scrubbing was chosen as a study case when evaluating the upgrading process with the data from the industrial biogas plants.

Table 5. The energy demands of the biogas upgrading process with different solvents.

Unit	H_2O	ConvIL1	NovIL1	NovIL2
Make-up solvent, t/h	0.71	0.33	0.15	0.12
Recirculated solvent, t/h	46	22	9.0	7.8
CO_2-OFFG, kmol/h	4.8	4.7	4.3	4.3
CH_4-OFFG, kmol/h	0.018	0.040	0.01	0.00015
CO_2-LIQCIR, kmol/h	0.00012	0.36	0.000044	0.0000034
CH_4-LIQCIR, kmol/h	0	0.00020	0	0
CO_2-GASCIR, kmol/h	2.5	3.7	1.5	0.66
CH_4-GASCIR, kmol/h	0.23	0.50	0.14	0. 013
Power, kW				
COMP 1	13	13	12	12
COMP 2	14	14	13	11
PUMP	15	6.6	4.0	3.7
VACUUM PUMP	-	7.5	-	-
BLOWER	3.6	-	3.6	3.6
Total	**46**	**41**	**33**	**30**
Total, kWh/ Nm^3 biogas	**0.20**	**0.18**	**0.15**	**0.13**

(b) Verification and comparison

In order to conduct the comparison of the simulation results with the industrial data, the energy usage, mainly electric power demand, was calculated based on the data collected from different industrial upgrading processes as kWh per Nm^3 of treated gas (Table 6). The energy usage for the industrial plants varied between 0.21 and 0.88 kWh/Nm^3.

In the process simulation, the raw gas flow rate data as well as the methane content in the raw gas collected from the industrial plants as listed in Table 4 were used in the IL upgrading simulation model in order to see the outcome on the energy usage for IL technique based on different industrial scenarios. The simulated result for the energy usage of water scrubbing technique, 0.20 kWh/Nm^3, was within the error bars of the average industrial data on water scrubber upgrading facilities, plants A, B, D and E (which was 0.41±0.27 kWh/Nm^3). In addition, the simulation corresponded well to the data given in literature for different upgrading techniques ranging from 0.2 to 0.3 kWh/Nm^3 [17].

The energy usage of the simulated case with IL-based technology (0.13-0.14 kWh/Nm^3) was further compared with the energy usage from the simulated water scrubbing upgrading process, and it was about 33% lower for IL-based technology. To be noted is that plant B had some operating issues with the upgrading process and currently not running the upgrading plant at full capacity, which potentially gives a less representative value for the average energy usage for the water scrubbing technique. When the calculations of the average energy usage are based only on plants A, D and E, the average is then 0.25±0.03 kWh/Nm^3, and this makes the energy usage of the simulated upgrading with ILs 46% lower than the industrial water scrubbing data and 77% lower than industrially applied membrane technology. Overall, the results indicate that NovIL2 scrubbing can have a positive effect on the energy balance from biogas production for vehicle fuels or for injection in the gas grid. However, it should be mentioned that the data from the industrial plants contains energy losses that are not included in the simulation model. It should also be noted that there are some uncertainties in the collected data regarding how the data is measured and what limitations are set when reporting the data.

Table 6. The collected energy usage of the different industrial upgrading plants and the energy usage of NovIL2 upgrading calculated from the simulation model with the input values from Table 4.

Plant	Upgrading technology	Energy usage of upgrading, *kWh/Nm*^{3}	Energy usage of NovIL2 upgrading, *kWh/Nm*^{3}
A	Water scrubbing	0.25	0.13
B	Water scrubbing	0.88	0.14
C	-	-	-
D	Water scrubbing	0.29	0.13
E	Water scrubbing	0.21	0.14
F	Membrane	0.58	0.13

(c) Sensitivity analysis of methane content and gas flow rate on energy usage

To investigate the effect of methane content and raw gas flow rate on energy balance of the NovIL2 scrubbing, a sensitivity analysis was performed based on the industrial data from Table 4. The simulation results are illustrated in Figure 6. It is apparent that under the conditions of AD with food waste, the energy usage does not vary much, but there is a difference of approx. 6% in energy usage of IL upgrading technology using raw gases produced from anaerobic digestion of ethanol stillage (50% CH_4 content) and from food waste (> 60% CH_4 content), where the latter requires less energy. As shown in Figure 6(b), assuming the methane content is 63%, the energy usage decreases with 7.2% when the raw biogas flow rate varies from 0.44×10^6 to 7.7×10^6 *Nm*^{3}*/year*. With increasing biogas flow rate up to 19 $\times$*10*^{6} *Nm*^{3}*/year*, the decrease of energy usage is not notable.

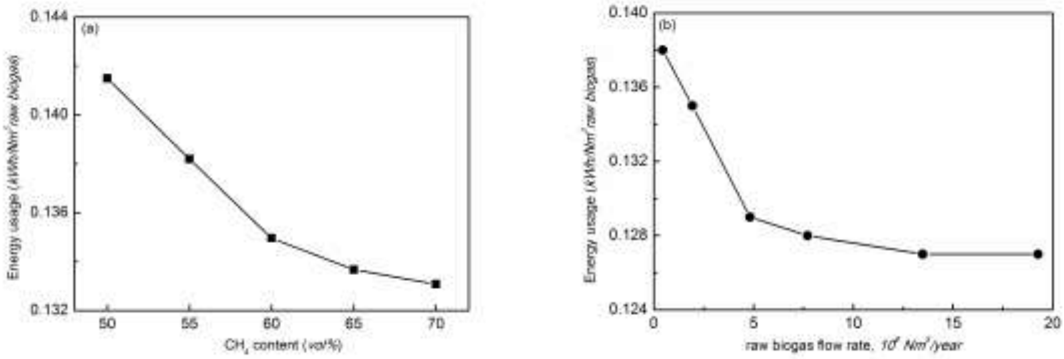

Figure 6. Effect of methane content in raw biogas (left) and raw biogas flow rate (right, 63% CH_4) on the energy usage.

4.2.3 Techno-economic evaluation

(a) Capital investment cost

NovIL2 scrubbing has the lowest power requirement and was chosen as a case also in the economic evaluation. The capital investment cost was calculated according to the information listed in Table 2 based on a capacity of 224 Nm^3/h. The f_{mp}, f_m and the purchased equipment costs (*PC*) for columns, heat exchangers and pumps can be referred to the values reported by Scholz *et al*. [11]. The calculated capital investment for the equipment is listed in Table 7, and the total capital cost was 932 kUSD (k$). Assuming an economic life of 15 years and an interest rate of 9%, the annual capital investment cost (*ACC*) was computed to be 116 k$/year. It was assumed that the annual operating time is 8 600 h. The annual operating cost was 260 k$/year, which is about 69% of the total upgrading cost.

Table 7. The capital investment cost for NovIL2 scrubbing from the simulation.

	absorber	desorber	flash	compressor	pump	blower	cooler	*EC*	*TCC*	*ACC*
Cost, kUSD(k$)	31	12	48	60	1.0	12	3.0	167	932	116

(b) Operation and maintenance cost (OMC)

Based on the collected industrial data, the operation and maintenance cost for the six industrial upgrading plants (A-F) varied from 0.064 to 0.81 $/Nm^3 raw gas for upgrading and 250-610 k$/year, Table 8. The operation and maintenance cost for the upgrading process at the industrial plants includes personnel, spare parts, energy, depreciation and other (including water and process aids). Similar to the observation for the energy usage, the cost varies a lot among the different industrial upgrading processes where plant B shows quite high cost per treated unit of raw gas which is again due to the fact that the upgrading process is not running at full capacity but still have almost the same portion of operation and maintenance dedicated to it as if it were running full time. Plant A shows a low cost per treated Nm^3 (0.064 $/Nm^3) and per year (250 k$/year). This is due to that plant A has depreciated their upgrading equipment but has normal cost levels besides that. Common to all the industrial plants is that depreciation constitutes a large part of the operation and maintenance cost.

The *OMC* for the simulated NovIL2 upgrading is 260 k$/year (0.13 $/Nm^3), which lies in the lower span of the cost data from the industrial plants. The OMC occupied about 69% of the total annual cost (*TAC*) as mentioned above. Compared to the values for the simulated water scrubbing process, the *OMC* for the NovIL2 upgrading decreases by 10%, although the electrical power decreases by around 35%. This is probably due to the fact that the electrical cost constitutes quite a small part of the operation and maintenance cost compared to the other costs, such as depreciation, which is related to the investment cost.

Table 8. The collected operation and maintenance cost for the upgrading at the industrial plants and the costs for the case with ILs from the simulations.

Plant	A	B	C	D	E	F	NovIL2 upgrading
Operation and maintenance cost ($/Nm^3)	0.064	0.81	-	0.13	0.24	0.37	0.13
Yearly operation and maintenance cost (k$/year)	250	350	-	610	410	280	260

4.3 PROJECT RESULTS DISSEMINATION

Part of the project results were presented at the yearly program conference of f3, on February 4th, 2016, in Gothenburg, Sweden. Part of the project results were presented at the 8th International Conference on Applied Energy (ICAE2016) held on October 8-11, 2016, in Beijing, China. Meanwhile, part of the project results have been discussed with FutureEco AB and a site visit has been arranged to Biogas Boden in order to know the current water-scrubbing technology and its challenge for further improvement. Part of the project results were used as preliminary results for CO_2 separation in steel-making and mining industries to present and discuss with the experts at SWEREA MEFOS.

Within the project, the following scientific publications have been prepared:

1. Yujiao Xie, Chunyan Ma, Xiaohua Lu, Xiaoyan Ji. Evaluation of ionic liquid-based technology for biogas upgrading. *Applied Energy*, 2016, 175: 69-81.
2. Yujiao Xie, Johanna Björkmalm, Karin Willquist, Johan Yngvesson, Chunyan Ma, Xiaoyan Ji. Evaluation of biogas upgrading using ionic liquids with the integrated anaerobic digestion process. *The 8th International Conference on Applied Energy – ICAE2016*, Beijing, China.
3. Yujiao Xie, Johanna Björkmalm, Chunyan Ma, Karin Willquist, Johan Yngvesson, Ola Wallberg, Xiaoyan Ji, Techno-economic evaluation of biogas upgrading using ionic liquids in comparison with industrially used technology in Scandinavian anaerobic digestion plants. *Applied Energy*, 2017. Available online 29 July.

5 CONCLUSION

In this cooperative project, three conventional ILs (ConvIL1, ConvIL2, ConvIL3) and two novel ILs (NovIL1, NovIL2) were chosen as liquid solvents for biogas upgrading in order to investigate how the properties of ILs affected the process performance in respect to commercial co-digestion facilities in Sweden and Norway. Their properties and the gas solubilities in these ILs were represented with the models embedded in Aspen Plus. After the implementation of the model parameters, the process simulation of biogas upgrading with these ILs was performed in Aspen Plus. The NovIL2 scrubbing was further simulated with input data from Swedish and Norwegian industrial biogas processes using different substrates. An economic evaluation was made for the NovIL2 upgrading process and was compared to the industrial data from upgrading plants and the data from literatures.

For the three studied conventional ILs, the investigation shows that the amount of recirculated solvents and the total energy usage for upgrading process using ILs follow: ConvIL1< ConvIL2< ConvIL3. The process with ConvIL1 was chosen as an example to perform the sensitivity analysis. The results show that the pressure drop in the absorber increases with increasing density and viscosity of solvent. The absorber diameter increases with increasing viscosity but changes slightly with increasing density. The CH_4 yield and CO_2 removal efficiency increase with increasing pressure in the absorber and the flash tank and decrease with increasing absorber temperature. The energy usage increases with increasing pressure and temperature in the absorber and decreases with increasing pressure in the flash tank.

The performance of the technology with the ILs (ConvIL1, NovIL1, and NovIL2) was further compared with water scrubbing. The comparison indicates that the IL technology is promising in respect to the amount of recirculated solvent and the total energy usage for the upgrading process, especially NovIL2 and NovIL1. The simulated result of energy efficiency and operational cost correspond well with the industrial data, showing the applicability of the model to simulate upgrading processes. The model shows that the greatest benefit of using IL technology is energy saving with a 35% saving in electricity, while the total capital cost (*TCC*) and the operation and maintenance cost (*OMC*) for the ConvIL2 upgrading decreases by 7% and 10%, respectively, compared to water scrubbing. In the situation where electricity price increases, the IL technology can be an interesting alternative to conventional water scrubbing technology. This is especially relevant to the anerobic digestion raw biogas upgrading since many plants are currently struggling with profitability.

6 FUTURE PROSPECTS

The research results show that ILs are promising candidates for biogas upgrading. The discussion with the industries, for example FutureEco AB, also gives us positive feedback to develop this technology together. More work will be carried out with the focus on the development of "second generation of ionic liquids" to further improve the performance.

7 APPENDIX: THERMODYNAMIC MODELLING

7.1 MODELING PROPERTIES OF IL'S

The critical properties (T_c, P_c, V_c, Z_c), normal boiling temperature (T_b) and acentric factor (ω) of ILs cannot be determined experimentally. In this work, the group contribution method proposed by Valderrama *et al.* was used to estimate these properties[18-19]. The methods are described as the following equations:

$$T_b = 198.2 + \sum n\Delta T_b \tag{A1}$$

$$T_c = \frac{T_b}{0.5703 + 1.0121\sum n\Delta T_c - (\sum n\Delta T_c)^2} \tag{A2}$$

$$P_c = \frac{M}{(0.2573 + \sum n\Delta P_c)^2} \tag{A3}$$

$$V_c = 6.75 + \sum n\Delta V_c \tag{A4}$$

$$Z_c = \frac{P_c V_c}{RT_c} \tag{A5}$$

$$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)} \log\left[\frac{P_c}{P_b}\right] - \frac{(T_c - 43)}{(T_c - T_b)} \log\left[\frac{P_c}{P_b}\right] + \log\left[\frac{P_c}{P_b}\right] - 1 \tag{A6}$$

In these equations, M is the molecular weight, T_c is the critical temperature, T_b is the normal boiling temperature, P_c is the critical pressure, and V_c is the critical volume. P_b is 1.01325 *bar* and R is 84.31 $bar \cdot cm^3/mol \cdot K$. The ΔT_c, ΔT_b, ΔP_c and ΔV_c are the contributions to the critical temperature, the normal boiling temperature, the critical pressure and the critical volume, respectively. The values of these contributions can be found in the literature [18-19]. n is the number of atoms or groups in the molecule.

The temperature-dependent properties (density, viscosity, surface tension and heat capacity) of ILs at atmospheric pressure were fitted to the following equations:

$$\rho_i = C_1 + C_2 T \tag{A7}$$

$$\ln \eta_i = C_1^{'} + C_2^{'}/T + C_3^{'} \ln T \tag{A8}$$

$$\sigma_i = C_1^{''}(1 - T/T_c)^{(C_2^{''} + C_3^{''}T/T_c)} \tag{A9}$$

$$C_{p,i} = C_1^{'''} + C_2^{'''}/T + C_3^{'''}T^2 \tag{A10}$$

where i refers to the component i, ρ_i is density, η_i is viscosity, σ_i is surface tension, $C_{p,i}$ is heat capacity, and C_1,C_2 and C_3 are the parameters of correlation.

The property of the mixture was correlated with the quadratic mixing rule in Aspen Plus. The equations are:

$$V_i = \frac{M_i}{\rho_i} \quad \text{(A11)}$$

$$V_{mix} = \sum_i x_i V_i + \sum_i x_i \sum_j x_j k_{ij} (V_i V_j)^{0.5} = \sum_i x_i V_i + V_i^E \quad \text{(A12)}$$

$$\ln \eta_{mix} = \sum_i x_i \ln \eta_i + \sum_i x_i \sum_j x_j l_{ij} (\ln \eta_i + \ln \eta_j) = \sum_i x_i \ln \eta_i + \Delta \eta_i \quad \text{(A13)}$$

$$A_i^E = RT \left[\ln(\eta_{mix} V_{mix}) - \sum_i x_i \ln(\eta_i V_i) \right] \quad \text{(A14)}$$

where V_i is the liquid molar volume, M_i is the molecular weight, V_{mix} and η_{mix} are the liquid molar volume and viscosity of the mixture. x_i is the mole fraction of each component, k_{ij} and l_{ij} are the binary parameters, and they were correlated from the corresponding experimental properties. V_i^E is the excess molar volume, $\Delta\eta_i$ is the viscosity deviation, and A_i^E is excess molar energy of activation.

The excess property (i.e. V^E, A^E) was fitted to Redlich–Kister equation [20]:

$$V_i^E = x_1 x_2 \sum_{n=0}^{4} A_n (x_1 - x_2)^n \quad \text{(A15)}$$

$$A_n = \sum_{i=0}^{1} a_i T^i \quad \text{(A16)}$$

where a_i is the parameter in fitting.

7.2 MODELING PHASE EQUILIBRIUM

(a) Pure-gas solubility in dry ILs

Due to the low vapor pressure of ILs, it was assumed that IL only exists in the liquid phase. The vapor-liquid equilibrium can be expressed as:

$$P\varphi_i = H_i x_i \gamma_i^* \quad \text{(A17)}$$

where P is the system pressure, $\varphi_{CO2}^{v}\varphi_i$ is the fugacity coefficient of gas i in the vapor phase, H_i is the Henry's constant of gas i in dry IL, x_i is the mole fraction of gas i in the liquid phase, γ_i^* is the activity coefficient of gas i in the liquid phase at the infinite dilution reference state.

The fugacity coefficient of gas i was calculated by the Redlich–Kwong (RK) equation [21]:

$$\ln \varphi_i = Z - 1 - \ln(Z - bP/RT) + \left(\frac{a/R^2 T^{2.5}}{b/RT} \right) \ln(1 + bP/ZRT) \quad \text{(A18)}$$

$$\begin{cases} P = \dfrac{RT}{V-b} - \dfrac{a}{T^{0.5}V(V+b)} \\ Z = PV/RT \\ a = 0.42748\dfrac{R^2T_{ci}^{2.5}}{P_{ci}} \\ b = 0.08664\dfrac{RT_{ci}}{P_{ci}} \end{cases} \quad \text{(A19)}$$

The critical temperature and pressure of CO_2 and CH_4 are 304.2 K, 7.38 MPa and 190.6 K 4.61 MPa.

The Henry's constant of gas *i* was expressed as:

$$H_i(T) = \lim_{P\to 0}(\frac{P\varphi_i}{x_i}) \quad \text{(A20)}$$

$$H_i(T,P) = H_i(T)\exp(\frac{PV_i^{\infty}}{RT}) \quad \text{(A21)}$$

$$\ln H_i(T) = h_1 + h_2/T + h_3\ln T + h_4/T^2 \quad \text{(A22)}$$

$$V_i^{\infty} = v_1 + v_2T \quad \text{(A23)}$$

where $H_i(T,P)$ is the Henry's constant of gas *i* at system temperature and pressure, $H_i(T)$ is the Henry's constant of gas *i* at zero pressure, and V_i^{∞} is the infinite dilution partial volume of gas *i* in the dry IL. h_1-h_4, v_1 and v_2 are the parameters of correlation.

The activity coefficient of gas *i* in the liquid phase was calculated by the Non-Random Two Liquids (NRTL) model [22]

$$\ln\gamma_i = \frac{\sum_{j=1}^{m}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{m}G_{li}x_l} + \sum_{j=1}^{m}\frac{G_{ij}x_j}{\sum_{l=1}^{m}G_{lj}x_l}\left[\tau_{ij} - \frac{\sum_{r=1}^{m}x_r\tau_{rj}G_{rj}}{\sum_{l=1}^{m}G_{lj}x_l}\right] \quad \text{(A24)}$$

$$\begin{cases} G_{ij} = \exp(-c_{ij}\tau_{ij}) \\ G_{ji} = \exp(-c_{ji}\tau_{ji}) \\ c_{ij} = c_{ji} \end{cases} \quad \text{(A25)}$$

where c_{ij} was assumed to be a certain value (i.e. 0-1), G_{ij}, G_{ji}, τ_{ij} and τ_{ji} are the binary interaction parameters and expressed as a function of temperature:

$$\begin{cases} \tau_{ij} = m_{ij} + n_{ij}/T \\ \tau_{ji} = m_{ji} + n_{ji}/T \end{cases} \quad \text{(A26)}$$

where m_{ij}, m_{ij}, n_{ij} and n_{ji} are the parameters correlated from the gas solubility.

(b) Gas solubility in aqueous ILs

For H_2O, the extended Raoult's law was used to represent the vapor-liquid equilibria, as shown in the following equation:

$$Py_w\varphi_w^v = x_w\gamma_w P_w^s \quad Py_w\varphi_w = x_w\gamma_w P_w^s \tag{A27}$$

where the subscript *w* refers to water, γ_w is the activity coefficient of water in the liquid phase, P_w^s is the saturated vapor pressure of water and calculated with the industrial standard IAPWS-IF97 within the range of 273.15 to 623.15 K [23].

For gas *i* (CO_2, CH_4), the vapor-liquid equilibrium in aqueous ILs was expressed as:

$$Py_i\varphi_i = H_{mix}x_i\gamma_i^* \tag{A28}$$

where y_i is the mole fraction of gas *i* in the vapor phase.

The Henry's constant of gas *i* in aqueous ILs (H_{mix}) was described as:

$$\ln H_{mix} = x_w \ln H_w + (1-x_w)\ln H_{IL} + \ln H^E \tag{A29}$$

The excess part of Henry's constant was expressed as:

$$\ln H^E = x_w(1-x_w)\sum_{n=0}^{1}(B_{n,1} + B_{n,2}T)(1-2x_w)^n \tag{A30}$$

where H_w and H_{IL} are the Henry's constants for gas in water and dry ILs, respectively. H_{mix} is the Henry's constant for gas in the mixture. $B_{n,1}$ and $B_{n,2}$ are the parameters fitted to the H_{mix} obtained from the experimental gas solubility in the aqueous ILs.

The activity coefficient of component *i* (γ_i) in the liquid phase was calculated with NRTL model. The fugacity coefficient of component *i* (φ_i) was calculated with the RK equation. For gas mixtures, the mixing rules for *a* and *b* in eq. 19 are $\sqrt{a} = \sum_i y_i\sqrt{a_i}$ and $b = \sum_i y_i b_i$

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