Towards novel biogas upgrading processes

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Åbo Akademi University 2013

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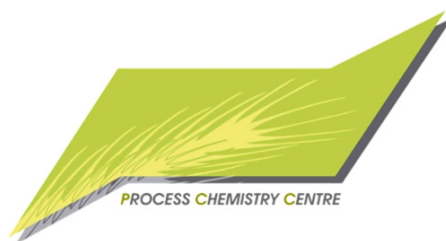D. Mendeleev University of Chemical Technology, Moscow, Russia

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Посвящается моим родителям

"All our dreams can come true – if we have the courage to pursue them."

Walt Disney

PREFACE

The present work was carried out at the Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Department of Chemical Engineering at Åbo Akademi University between 2008 and 2012. This research is a part of the activities at the Åbo Akademi University Process Chemistry Centre within the Finnish Centre of Excellence Program (2000-2011) appointed by the Academy of Finland. Furthermore, the Academy of Finland Sustainable Energy programme, the Finnish Agency for Technology and Innovation (TEKES) and the Bio4Energy programme are gratefully acknowledged for financial support. COST CM0903 ('UBioChem') is also acknowledged.

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I would like to acknowledge all the co-authors and co-workers I had the pleasure to work with. Special thanks for their contribution go Mrs. Elena V. Murzina and Dr. Mari Nurmi. Erno Karjalainen is acknowledged for his assistance in the work devoted to poly(ionic liquid)s. I greatly appreciate Dr. Saija Rasi's assistance in my work with biogas samples and would like to say thank you for the delightful time I spent in Jyväskylä.

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I was fortunate to have Vladislav Lashko as my very first English language tutor and deeply appreciate his extraordinary talent for teaching the language, pushing me and taking an interest in my success. I am eternally grateful to you, because you really have widened my horizons like no one else.

Elena I. Privalova
Åbo/Turku, January 2013

ABSTRACT

Elena Privalova

Towards novel biogas upgrading processes.

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Keywords: biogas upgrading, CO_2 capture, amine solutions, piperazine, ionic liquids, poly(ionic liquid)s, 'switchable' ionic liquids, regeneration, viscosity, volatile organic compounds (VOCs).

Biogas production has considerable development possibilities not only in Finland but all over the world since it is the easiest way of creating value out of various waste fractions and represents an alternative source of renewable energy.

Development of efficient biogas upgrading technology has become an important issue since it improves the quality of biogas and for example facilitating its injection into the natural gas pipelines. Moreover, such upgrading contributes to resolving the issue of increasing CO_2 emissions and addresses the increasing climate change concerns. Together with traditional CO_2 capturing technologies a new class of recently emerged sorbents such as ionic liquids is claimed as promising media for gas separations.

In this thesis, an extensive comparison of the performance of different solvents in terms of CO_2 capture has been performed. The focus of the present study was on aqueous amine solutions and their mixtures, traditional ionic liquids, 'switchable' ionic liquids and poly(ionic liquid)s in order to reveal the best option for biogas upgrading. The CO_2 capturing efficiency for the most promising solvents achieved values around 50 - 60 L CO_2 / L absorbent. These values are superior to currently widely applied water wash biogas upgrading system.

Regeneration of the solvent mixtures appeared to be challenging since the loss of initial efficiency upon CO_2 release was in excess of 20 - 40 vol %, especially in the case of aqueous amine solutions. In contrast, some of the ionic liquids displayed reversible behavior. Thus, for selected "switchable" ionic and poly(ionic liquid)s the CO_2 absorption/regeneration cycles were performed 3 - 4 times without any notable efficiency decrease.

The viscosity issue, typical for ionic liquids upon CO_2 saturation, was addressed and the information obtained was evaluated and related to the ionic interactions.

The occurrence of volatile organic compounds (VOCs) before and after biogas upgrading was studied for biogas produced through anaerobic digestion of waste waters sludge. The ionic liquid [C_4mim][OAc] demonstrated its feasibility as a promising scrubbing media and exhibited high efficiency in terms of the removal of VOCs. Upon application of this ionic liquid, the amount of identified VOCs was diminished by around 65 wt %, while the samples treated with the aqueous mixture of 15 wt % N-methyldiethanolamine with addition of 5 wt % piperazine resulted in 32 wt % reduction in the amounts of volatile organic compounds only.

REFERAT

Elena Privalova

Utveckling och jämförelse av nya biogasuppgraderingsprocesser

Doktorsavhandling, Teknisk kemi och reaktionsteknik, Processkemiska centret, Insitutionen för kemiteknik, Åbo Akademi, 2013.

Nyckelord: biogasuppgradering, CO_2-upptagning, aminlösningar, piperazin, joniska vätskor, polyjoniska vätskor, 'switchable' joniska vätskor, regenerering, viskositet, flyktiga organiska föreringar (VOC).

Produktionsprocesser för biogas har många utvecklingsmöjligheter i dagens läge, inte enbart i Finland utan även globalt, eftersom rötning av biomassa till biogas eventuellt är den lättaste vägen att skapa mervärde ut av olika reststömmar och samtidigt erbjuda en alternativ, förnyelsebar energikälla.

Utveckling av effektiva biogasuppgraderingsteknologier har blivit allt mera viktigt på sistone, eftersom den producerade biogasen med bättre kvalitet kan vid behov injiceras i existerande naturgasnätverk. Samtidigt bidrar dessa teknologier till att lösa problematiken kring utökade koldioxidemissioner av mänskligheten och den resulterande klimatförändringen. Tillsammans med de traditionella teknologierna för koldioxid-upptagning har nya typer av alternativa sorptionsmedia, såsom joniska vätskor, på sistone väckt uppmärksamhet som lovande matris för gasseparationer.

I denna avhandling har en jämförelse av prestandan för olika sorptionslösningar studerats med hänsyn till koldioxidupptagning i en återcirkulationsreaktor samt i en satsvis reaktor. Fokus för detta arbete ligger på olika amin-vattenblandningar, 'traditionella' joniska vätskor, 'switchable'-joniska vätskor samt polyjoniska vätskor med målsättningen att identifiera det bästa alternativet för uppgradering av biogas. Upptagningsförmågan hos de bästa lösningarna uppgick till 50-60 liter CO_2/liter upplösningsmedia – ett värde som vida överstiger dagens typiska teknologi, vattentvätt, vid uppgradering av biogas.

Regenerering av sorptionslösningarna konstaterades vara uppmanande, eftersom många system tappade 20-40 volym% av kapaciteten i samband med det första sorptionscykeln. Detta var fallet i synnerhet vid användning av amin-vattenblandningar. Som motsats till detta uppvisade vissa joniska vätskor reversibla egenskaper. I själva verket konstaterades att åtminstone 3-4 återcirkuleringsförsök kunde utövas utan en nämnvärd minskning i kapaciteten för några 'switchable' joniska vätskor samt polyjoniska vätskor.

Vidare, problemet med höga viskositeter vanliga vid CO_2-mättning av joniska vätskor tacklades och ny information samlades för att evaluera inverkan av de joniska sammankopplingarna.

Uppkomsten av flyktiga organiska föroreningar (VOCs) kontrollerades både i rå biogas härstammande från anaerobisk rötning av avfallsvattenslam och i uppgraderad biogas. Joniska vätskan [C_4mim][OAc] uppvisade god prestanda och hög kapacitet vid absorption av dessa föreningar. Vid uppgraderingsförsök med denna joniska vätska observerades en förminskning i mängden av identifierade organiska föroreningar som motsvarar 65 vikt-% i jämförelse till fallen då en 15 vikt- % N-metyldietanolamin (i vatten) tillspetsad med 5 vikt-% piperazin användes, varvid enbart 32 vikt-% av organiska föroreningar kunde avlägsnas.

Реферат

Привалова Елена Ивановна

Новые возможности для улучшения качества биогаза

Производство биогаза располагает огромным потенциалом для развития не только в Финляндии, но и во всем мире, поскольку в результате переработки органических отходов получается био-метан - альтернативный источник возобновляемой энергии.

В последнее время особый интерес уделяется разработке методов удаления различных примесей из биогаза, поскольку это способствует повышению его качества и позволяет осуществлять соединение с трубопроводами природного газа.

Более того, разработка системы повышения качества биогаза и, в частности, удаления углекислого газа, способствует уменьшению его выбросов в атмосферу. Наряду с распространенными в промышленности методами поглощения углекислого газа применение нового класса химических реагентов, ионных жидкостей, вызывает повышенный интерес в качестве альтернативной среды разделения различных соединений без взаимного загрязнения.

В данной работе рассматривались различные сорбенты для разделения газов с точки зрения их возможностей для удаления CO_2. Оценка их эффективности проводилась с помощью реакторов периодического и непрерывного действия. Основное внимание было уделено водным растворам аминов в связи с их широким использованием в современных процессах удаления углекислого газа из топочных газов и в процессах очистки в промышленном производстве аммиака и водорода. В качестве альтернативы рассмотрены различные представители ионных жидкостей, а именно, традиционные ионных жидкости, полимеры на основе ионных жидкостей и CO_2-связывающие растворители, работающие по принципу "переключаемого" растворителя Джессопа. Поглотительная способность наиболее эффективных сорбентов достигала 50 - 60 литров углекислого газа на литр раствора. Более того, в ходе работы проводилось сравнение рассматриваемых растворителей с традиционными методами удаления углекислого газа.

Регенерация отработанных растворителей подчас проблематична, так как после удаления углекислого раза растворитель теряет свою эффективность на 20 - 40 об. %, что особенно характерно для водных растворов аминов. В отличие от аминных растворов, ряд ионных жидкостей продемонстрировал способность легко регенерироваться. В частности, была проведена серия циклов поглощения и высвобождения CO_2 для полиионных жидкостей и "переключаемых" ионных

жидкостей, которая показала их способность к регенерации без потери активности и подтвердила возможность многократного использования.

Особое внимание было уделено проблеме увеличения вязкости ионных жидкостей в ходе поглощения молекул углекислого газа, так как такое увеличение значительно ограничивает их области применения. Полученные данные позволяют оценить силу взаимодействия между ионами в растворе.

Был проведен анализ биогаза, полученного в результате анаэробного (без кислорода) брожения сточных вод, чтобы установить наличие различных летучих органических веществ (ЛОВ) и степень их удаления в процессе обработки различными растворами. Применение ионной жидкости 1-н-бутил-3-метилимидазолия ацетат [C$_4$mim][OAc] подтвердило возможность ее использование для удаления летучих органических веществ. В случае применения данной ионной жидкости концентрация ЛОВ снижалась на 65 вес. %, в то время как обработка образца биогаза раствором аминов, содержащим 15 вес. % N-метилдиэтаноламина и 5 вес. % пиперазина, способствовала снижению концентрации ЛОВ только на 32 вес. %.

Таким образом, данная работа вносит существенный вклад в развитие нового процесса улучшения качества биогаза, основанного на применении различных ионных жидкостей и дает первичную сравнительную характеристику таких важных факторов как адсорбционная емкость сорбентов, их регенерация и повторное использование, увеличение вязкости в процессе очистки и степень удаления летучих органических веществ. Дальнейшие исследования в данной области приведут к созданию экономически эффективной технологии с минимальным экологическим риском.

LIST OF PUBLICATIONS

The thesis consists of the following papers, which are referred to in the text by their Roman numerals.

I. E. I. Privalova, P. Mäki-Arvela, D. Yu. Murzin, J.-P. Mikkola. Capturing CO_2: Conventional versus ionic-liquid based technologies. *Russian Chemical Review*, 81 (5), 435-457 (2012).

II. E. Privalova, S. Rasi, P. Mäki-Arvela, K. Eränen, J. Rintala, D. Yu. Murzin, J.-P. Mikkola. CO_2 capture from biogas: absorbent selection. *RSC Advances,* 3, 2979-2994 (2013).

III. E. Privalova, P. Mäki-Arvela, K. Eränen, A. K. Avetisov, J.-P. Mikkola, D. Yu. Murzin. Amine solutions for biogas upgrading: ideal vs. non-ideal absorption isotherms *Chem. Eng. Technol.* (accepted).

IV. E. Privalova, M. Nurmi, M. S. Marañón, E. V. Murzina, P. Mäki-Arvela, K. Eränen, D. Yu. Murzin, J.-P. Mikkola. CO_2 removal with 'switchable' versus 'classical' ionic liquids. *Sep. Purif. Technol.* 97, 42-50 (2012).

V. E. Privalova, E. Karjalainen, M. Nurmi, P. Mäki-Arvela, K. Eränen, H. Tenhu, D. Yu. Murzin, J.-P. Mikkola. Imidasolium-based poly(ionic liquid)s as a new alternative for CO_2 capture. *ChemSusChem*. (submitted)

VI. E. Privalova, S. Rasi, K. Eränen, D. Yu. Murzin, J.-P. Mikkola. Ionic liquids vs. amine solutions in biogas upgrading: the level of VOCs. *Biofuels* (accepted).

Author's contribution

All the experiments were planned and performed by the author, except SEM, DSC and viscosity measurements. Some of the experiments in the paper (IV) were carried out by M. S. Marañón and E. V. Murzina under supervision of the author. All the first drafts of the manuscripts were written by the author and finalized together with the supervisors. Synthesis and partly characterization of polyionic liquids (VI) was performed by the co-authors from University of Helsinki. The part related to synthesis and characterization of poly(ionic liquid)s in the article (VI) was written by E. Karjalainen.

OTHER PUBLICATIONS RELATED TO THE TOPIC

I. E. Privalova, P. Mäki-Arvela, K.Eränen, D. Yu. Murzin, J.-P. Mikkola. CO_2 capture from biogas: reactor and solvent selection, *19th International Congress of Chemical and Process Engineering CHISA & 7th European Congress of Chemical Engineering-ECCE-7,* August 2010, Prague, Czech Republic, oral presentation.

II. E. Privalova, M. S. Marañón, P. Mäki-Arvela, K. Eränen, D. Y. Murzin, J.-P. Mikkola. Comparison of CO_2 capture capacity of RTILs and SILs, *Green Solvents for Synthesis*, October 2010, Berchtesgaden, Germany, poster presentation.

III. E. Privalova, P. Mäki-Arvela, K. Eränen, D. Y. Murzin, J.-P. Mikkola. Comparison of conventional and novel absorbents for CO_2 capture, *11th International Conference on Carbon Dioxide Utilization,* June 2011, Dijon, France, poster presentation.

IV. E. Privalova, P. Mäki-Arvela, M. Nurmi, K.Eränen, D. Yu. Murzin, J.-P. Mikkola. CO_2 removal with 'switchable' solvents versus ionic liquids, *1st International Conference on Ionic Liquids in Separation and Purification Technology,* September 2011, Sitges, Spain, oral presentation.

V. S. Hyvärinen, E. Leino, V. Eta, E. Privalova, E. Salminen, J. Grasvic, P. Virtanen, P. Mäki-Arvela, J-P. Mikkola, Book Chapter, Ionic liquids as Catalytic Medium for Biomass Transformation, in 'Heterogeneous catalysis in Biomass to Chemicals and Fuels,' Ed. Dr. D. Kubicka, Czech Rep, 2011.

VI. E. Privalova, P. Mäki-Arvela, K.Eränen, D. Yu. Murzin, J.-P. Mikkola. Assessing alternatives for biofuel upgrading, *CAT4BIO Conference. Advances in Catalysis for Biomass Valorization*, July 2012, Thessaloniki, Greece, poster presentation.

CONTENTS

1. INTRODUCTION

1.1 Biogas as alternative renewable energy source

Nowadays, biogas is recognized as a valuable alternative energy resource frequently utilized in heat and electricity production. Biogas formation is based on biological decomposition of organic raw materials. Thus, the composition of biogas depends on process conditions and the raw materials applied, such as landfills, sewage sludge or other bio-waste. Typical biogas production plants generate a gas containing 40 - 60 vol % of bio-methane and 25 - 45 vol % of carbon dioxide [1].

Carbon dioxide is considered as a greenhouse gas and is often assigned as being responsible for global warming [2]. Carbon dioxide should be removed from the biogas to increase its heating value, decrease the transportation costs and avoid the corrosion in pipelines. In the case of more refined use of bio-methane (e. g. transportation fuel, chemical synthesis), purification is also a must.

Besides carbon dioxide, biogas often contains various other contaminants such as sulphur compounds, organic silicon compounds, halogenated hydrocarbons, aromatics, oxygenated compounds and other residual species which have detrimental environmental effects, facilitates corrosion problems and damage engine surfaces [3].

However, the research in the field of biogas upgrading has gained little attention during the last years even if there is growing attention to the production of biogas in general (Fig. 1).

Among the major biogas upgrading technologies water scrubbing, pressure swing adsorption (PSA), membrane separation and cryogenic separation can be listed. Pressurized water wash scrubbing belongs to the one most frequently used since it seems to be the cheapest option, although the efficiency of water for CO_2 capture is still rather limited compared to organic solvents. The schematic view of biogas upgrading based on an absorption process is shown in Figure 2.

Thus, the development of a novel absorption media with desired requirements will contribute to effective scrubbing applications, decreasing the energy consumption, investment and operational costs. Novel innovative upgrading processes should facilitate more efficient biogas utilization and integration in the present energy infrastructure.
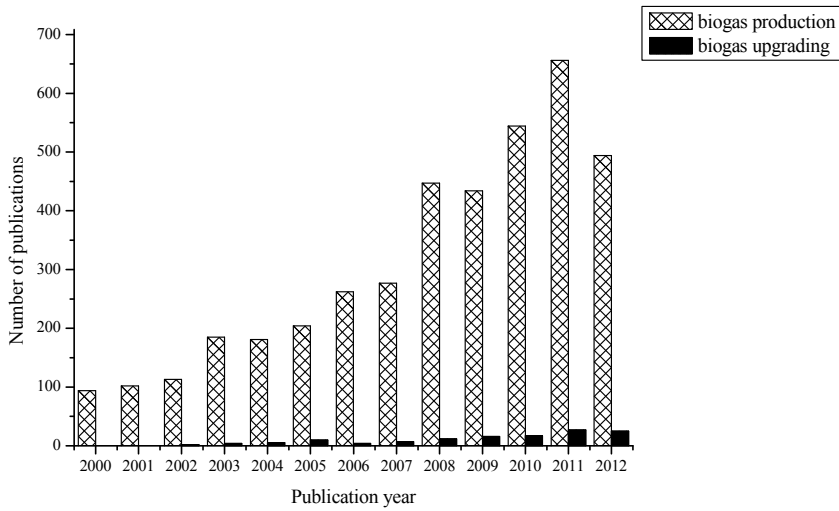
Figure 1. Historical trends in the number of publications per year, reporting the concepts "biogas production" and "biogas upgrading", available in open literature (SciFinder®, as entered, English only, December 2012).
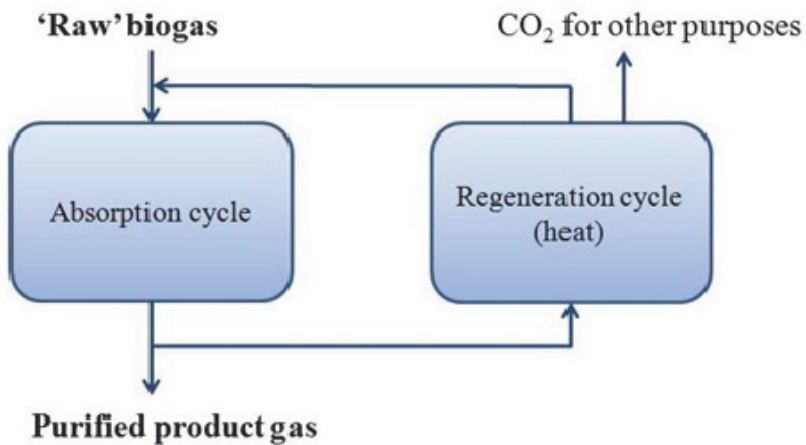
Figure 2. Schematic view of a gas upgrading process.

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1.2 Conventional technologies for CO_2 capture

Recently, much research effort has been dedicated towards CO_2 capture [4]. As a result, many new absorption solutions have been developed [5] and tested in terms of CO_2 capture (Fig. 3).
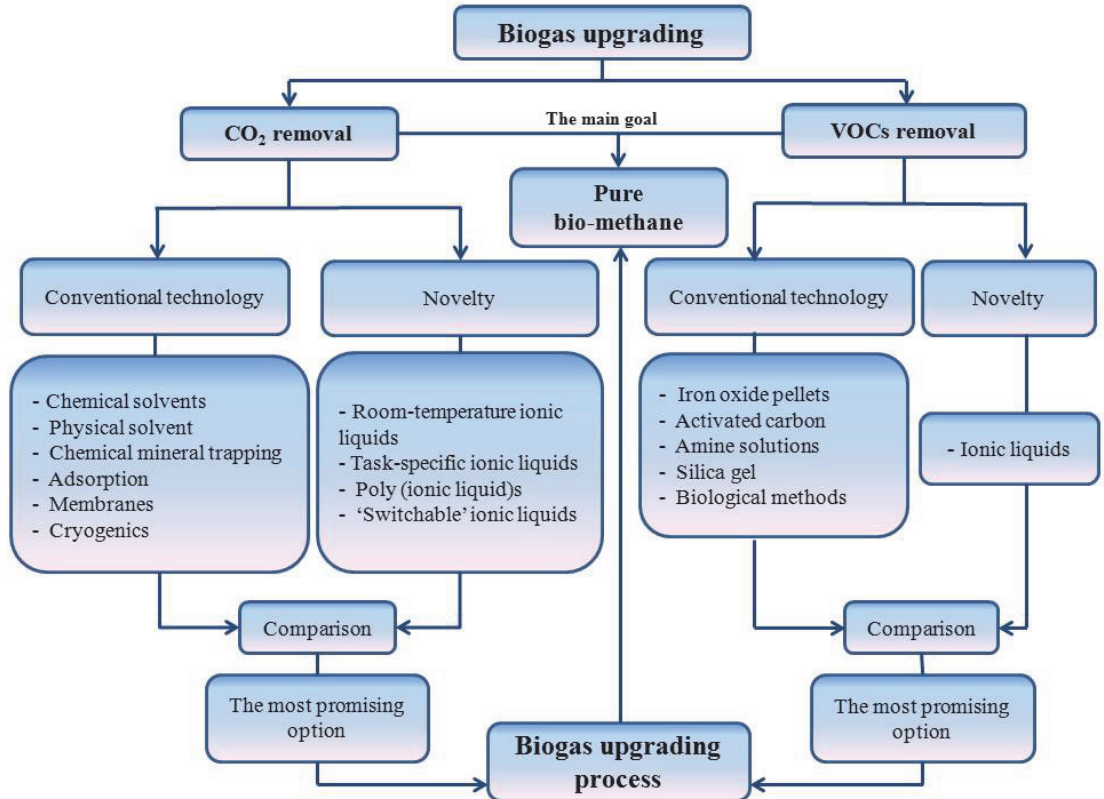
Figure 3. Overview of biogas upgrading process and research strategy.

Owing to their high capacity, CO_2 capture with aqueous amine solutions seems to be the leading industrial technology [6]. However, the use of monoethanolamine in the MEA-based process, applied for a long time as the dominant approach, is associated with several disadvantages, such as high energy consumption at the regeneration step, corrosivity and degradation problems [7]. BASF activated 'aMDEA' process based on

the application of N-methyldiethanolamine (MDEA) with piperazine (PZ) as an activator is claimed to cope with the abovementioned issues [8]. Moreover, aMDEA is considered to be non-toxic and non-corrosive and, therefore, environmentally friendly sorbent.

While amine scrubbing belongs to the class of chemical solvent scrubbing, the properties of aMDEA vary depending on the PZ concentration and can be shifted to behave more like a physical solvent. The possibility to combine the advantages of chemical and physical solvents expands the process flexibility [9].

Moreover, several industrial processes apply chemical solvents such as aqueous ammonia solutions, aqueous potassium and sodium carbonate and their mixtures with amines and physical solvents [5]. Among the most widely known are the Benfield (UOP), Catacarb (Eickmeyer), LRS10 (British Gas), Flexsorb HP (ExxonMobil) and Giammarco-Vetrocoke processes [10, 11].

Physical absorbents are usually favorable for the separation of the gas mixtures containing high partial pressure of CO_2. The main physical solvents used for CO_2 removal are cold methanol (Rectisol/ Lurgi and Linde), N-methyl-2-pyrrolidone (Purisol/Lurgi), dimethyl ether of polyethylene glycol (Selexol/UOP) as well as propylene carbonate (Fluor Solvent process/Fluor Daniel) [10, 11].

The primary advantage of physical sorbents over chemical ones is their lower energy requirement since no chemical reaction is involved and CO_2 capture is accomplished via physical solubility interactions. CO_2 release can be achieved by means of pressure reductions (flash stages) [12]. However, the process also has several disadvantages, namely low CO_2 capacity, absorption of hydrocarbons, solvent loss and requirement of high circulation rates resulting in higher operating costs [7].

Moreover, another attractive option for CO_2 removal from oxygen-rich gas streams should be mentioned here. Amino acids and amino-acid salts are claimed to be suitable for this task and considered to be non-toxic and environmentally friendly [13, 14]. A high absorption rate and high selectivity for CO_2 capture as well as better resistance to degradation were claimed. Nonetheless, the energy requirements for solvent regeneration are reported to be higher compared to MEA and raise therefore concerns about applicability of these sorbents [14].

Thus, the recent CO_2 capturing technologies have certain limitations, and, consequently, it would be desirable to develop a CO_2 removal process merging the best characteristics and minimize substantial drawbacks of the numerous strategies available.

1.3 Novel sorbents

Ionic liquids (ILs) have been identified as new alternatives for CO_2 removal from gas streams [15]. As potentially "green" solvents, ionic liquids are offering the promise of minimized waste streams and are currently under intensive research [16]. Due to their unique properties, in particular, low vapour pressure, non-flammability and high thermal stability, they have attracted much interest being applied in different applications [17].

Ionic liquids consist of a large organic cation and a smaller organic/inorganic anion. The properties of room-temperature ionic liquids can in general be modified through varying cation-anion moieties.

The solubility of CO_2 in a "physical IL" involves the interactions between CO_2 and IL anion by means of weak Lewis acid-base interactions. This suggests that the nature of anion plays the key role here, while the cation plays a secondary role whereas the CO_2 solubility is slightly affected by increasing the alkyl chain length [16]. Among intermolecular interactions, van der Waals forces belong to the dominant ones and contribute most to the CO_2 dissolution. The electrostatic interactions have a less important contribution, whereas the effect of hydrogen bonding can be insignificant [16].

CO_2 uptake by a "chemical ionic liquid" 1-butyl-3-methylimidazolium acetate [C_4mim][OAc] is, presumably, accomplished through the generation of an intermolecular complex [18] or a chemical reaction leading to the carboxylation of the imidazolium ring accompanied by acetic acid formation [19].

The performance of ionic liquids can be significantly improved by means of incorporation of an amine function in the structure of the ionic liquid (task-specific ionic liquid) [20].

However, ionic liquids also possess several disadvantages limiting their practical usability, such as frequent high viscosity, low and difficult to control purity, and multistage synthesis procedure resulting in comparatively high prices. Poor knowledge about their toxicity and biodegradability impede the expansion of their practical scope.

While the majority of room-temperature ionic liquids remain liquid over a wide temperature range, the ionic liquids in polymeric forms are solids [21]. Many of them exhibit substantially increased CO_2 sorption capacity and demonstrate very high sorption/desorption rates compared to their corresponding monomers. In a few minutes the polymers such as poly[(p-vinylbenzyl)trimethylammonium hexafluorophosphate] P[VBTMA][PF$_6$] [22], poly[(p-vinylbenzyl)trimethylammonium tetrafluoroborate] P[VBTMA][BF$_4$] and poly[(2-(methacryloyloxy)ethyl)trimethylammonium tetrafluoroborate] P[MATMA][BF$_4$] [23] reached the equilibrium and complete CO_2 saturation. In contrast to room-temperature ionic liquids, in the case of IL-polymers the cation is assigned to be decisive upon CO_2 sorption [22]. These polymers are claimed to be reversible and CO_2 selective that renders them exceptionally promising for CO_2 separation as sorbents as well as membrane materials.

Recently, a new class of ionic liquids called 'switchable' solvents has emerged [24]. A mixture of an amidine or guanidine, for example 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), coupled with an (amino) alcohol can form ionic liquids upon CO_2 bubbling (Fig. 4) and revert back to non-ionic form by exposing to nitrogen or other inert gas [25]. More generally, an organic superbase (such as 1, 5-diazabicyclo(4.3.0)non-5-ene (DBN) or tetramethylguanidine) coupled with an OH-group containing molecule also forms ionic liquids [26].

8-diazabicyclo[5.4.0]undec-7-ene (DBU)
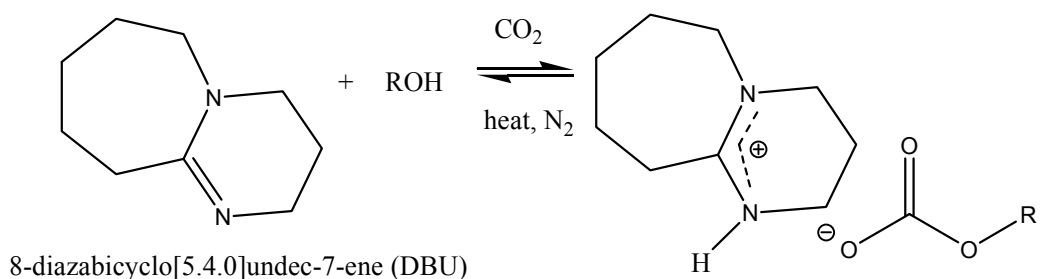
Figure 4. Reversible process of CO_2 binding by a 'switchable' ionic liquid.

The properties of such solvents can be tuned by varying the alcohol/base pair [27]. These solvents exhibit high CO_2 absorption performance and can be easily recycled [28].

The fact that no cumbersome organic synthesis is required is highlighted as one of the advantages compared to traditional ionic liquids. At the same time, the main disadvantage is the dramatically increased viscosity upon saturation with CO_2.

In order to develop a mixture with desirable properties, ionic liquids can be mixed with conventional solvents aiming at combining the tunable green properties of ionic liquids and the high efficiency of amines [29]. Such IL/amine mixtures exhibited better process flexibility and were effective at a range of pressures [30]. Thus, they combine the advantages of different solvents omitting some drawbacks [30]. For example, the viscosity issue typical for ionic liquids was significantly diminished upon mixing with amine solutions.

To summarize, much data was compiled from the literature on the various CO_2 capturing technologies operated under different conditions. However, a fair comparison is until today missing. Moreover, there is a lack of information on utilization, viscosity and regeneration characteristics for the emerging solvents intended to be used in industrial applications and, in particular, in biogas upgrading.

1.4 Aim and scope of the research

The overall objective of this research was to study the use of the emerging solvents in terms of their CO_2 capturing capacity and their applicability and efficiency in biogas upgrading. The long term goal is to develop a new sustainable, energy efficient and economically competitive technology.

An overview of the conventional CO_2 capturing technologies was performed in article **(I)**. A realistic comparison of different types of solvents claimed to be efficient with respect to their CO_2 loading capacity was made in paper **(II)**. Moreover, the work provides data on the absorbent regeneration and viscosity, crucial for economic process evaluation **(II)**. Utilization of activated MDEA solution upon biogas upgrading was studied in regard to the theory of intermolecular interactions between the absorbed molecules **(III)**.

Novel classes of solvents such as 'switchable' ionic liquids **(IV)** and poly(ionic liquid)s **(V)** were investigated in terms of their CO_2 capturing capacity. Furthermore, the occurrence of volatile organic compounds (VOCs) in biogas was confirmed and identified **(VI)**. The impact of chosen solvents on the level of VOCs removal was investigated **(II, VI)**.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Chemicals

The gases CO_2 (99.99 %), CH_4 (99.95 %) and N_2 (99.99 %) were obtained from AGA Oyj (Finland). Monoethanolamine (MEA) ($\geq$99.0 %), diethanolamine (DEA) ($\geq$99.5 %), N-methyldiethanolamine (MDEA) ($\geq$99.0 %), amino-2-propanol (AMP) (93.0 %), piperazine (PZ) (anhydrous, $\geq$99.0 %), polyethylene glycol 400 dimethyl ether (PEG), L-alanine ($\geq$99.5 %), β-alanine ($\geq$99.0 %), sarcosine ($\geq$98.0 %), L-asparagine (98.0 %), DL-serine ($\geq$99.0 %), glycine ($\geq$99.0 %), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) ($\geq$99, 0 %), 1-hexanol ($\geq$99.0 %), 4-amino-1-butanol (98 %), 6-amino-1-hexanol (97.0%), and 1-butyl-3-methylimidazolium acetate ([C_4mim][OAc]) ($\geq$95.0 %) were purchased from Sigma-Aldrich while the amino alcohols, L-prolinol (95.0%) and L-(+)-valinol (97.0 %), were purchased from ABCR. All chemicals were used without further purification. The ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] and 1-butyl-3-methylimidazolium dicyanamide [C_4mim][DCA] were synesized at M. V. Lomonosov Moscow State University (Russia) and analyzed by means of proton NMR spectroscopy **(II)**. All chemicals were used as received.

The poly(ionic liquid)s were prepared at the University of Helsinki by free radical polymerisation. Their structure was confirmed by means of proton NMR spectroscopy **(V)**.

2.1.2 Biogas

Biogas was obtained from BIOvakka's biogas plant (BIOvakka Suomi Oy, Topinoja, Åbo - Turku, Finland), where it is being produced in two 3500 m^3 digester tanks (Fig. 5).

Raw materials are charged to a storage tank (40m^3) through the receiving silo located in the open air (1). Thus, the sludge is in contact with air only for an hour, after which it is diluted with water and supplied to the underground storage tank (2) with the volume of 120 m^3 where slurry creation takes place. Then the slurry is pumped to the sludge storage 3 (800m^3). Passing a pulper buffer (4), the sludge flow splits into three

parallel flows leading to the reactors (5, 6, 7) with the volume of 10 m^3 each. In the reactor, 6 m^3 are taken by the sludge mixture and 4 m^3 are assigned for the gas phase. Due to the steam injection at this stage, the process of thermal hydrolyzation and sterilization begins at 3.5 bar and 130 ˚C.
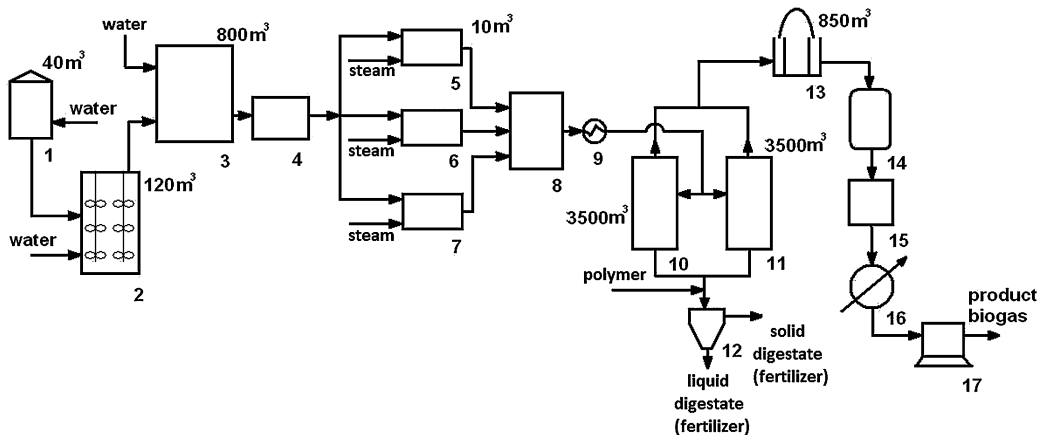
Figure 5. Biogas plant flowsketch, where 1 - storage tank; 2- underground storage tank; 3- sludge storage; 4 - pulper buffer for sludge; 5, 6, 7 – reactors; 8 - flash tank; 9 - heat-exchanger; 10, 11 – digesters; 12 - decanter centrifuge; 13- gas holder; 14- droplet separator; 15- active carbon filter; 16 – cooler; 17- compressor.

The system with three reactors was developed to handle more sludge per hour. To be able to release the excess pressure, there is a connection line to the pulper, which is also used to pre-heat the slurry. Then the effluents enter the flush tank 8 (16 m^3) which operates at the temperature of ca. 120 ˚C and at a pressure of ca. 0.3 bar. The cooling of the suspension down to 56 ˚C is performed before it enters the digesters by means of heat exchangers (9). The biogas is formed in the digesters (10, 11) at 53 ˚C and at the pressure of 23 mbars. Usually the digestion process takes 15 - 18 days. The overhead product gas from the digesters is combined in the line and led to a gas holder (850 m^3). Then it passes through the water removal section, active carbon filter, cooler (2 ˚C) and is pressurized to 200 mbars. The slurry coming from the bottom of the digester is mixed with the polymer and led to the decanter centrifuge, where it separates into solid and liquid fractions.

Raw biogas samples were withdrawn from an outlet collector pipe, where the product biogas was being collected after passing through water removal as well as active carbon filtres, cooling and pressurization stages.

The resulting raw biogas was, consequently, compressed into a gas storage tank by means of Makita AC310H 240V High Pressure Air Compressor 2.5HP. The biogas samples were obtained from the site in February 2010 and in June 2012, respectively.

2.2 Reactor systems

2.2.1 Loop reactor

A loop reactor with the liquid phase volume of 50 ml was designed, constructed and utilized for CO_2 capture from biogas and its model mixture (Fig. 6). In the latter case methane – carbon dioxide mixture containing 20 vol % of each gas was introduced into the reactor.
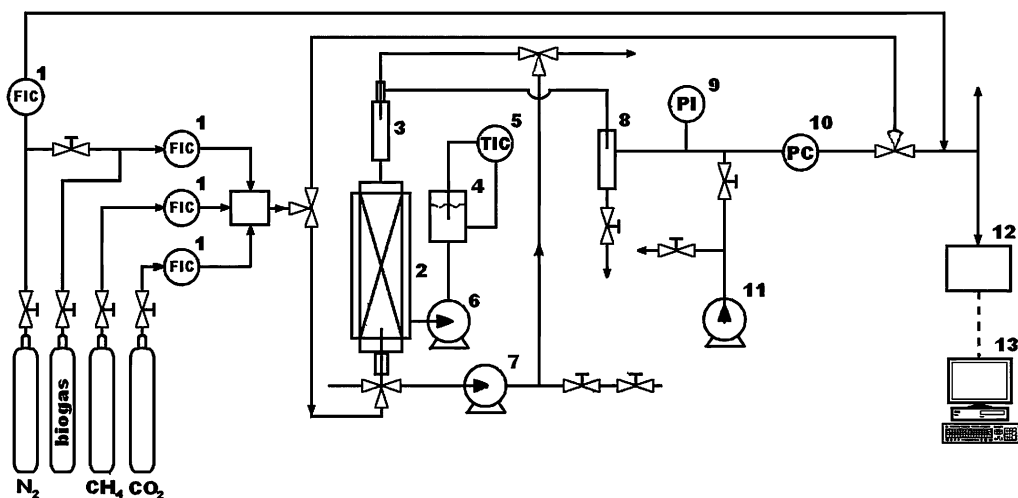
Figure 6. The reactor system with liquid phase volume V_L= 50 m: [1] - mass flow controller; [2] - absorption column; [3] - separator; [4]- thermostat; [5] – temperature controller; [6], [7] - peristaltic pumps; [8] - trap; [9]- pressure indicator; [10] – pressure controller; [11]- vacuum pump; [12] - gas analyser; [13]- computer.

The carrier gas was nitrogen. The gas stream was contacted counter-currently with various solvents. The gas flows were controlled by the flowmeters FlowPlot V 4.58 provided by Bronkhorst High-Tech B.V.

The CO_2 loading measurements were carried at different temperatures (8 - 50 ºC) and partial pressures of CO_2 between 1 and 5 bars. The temperature was measured with a thermocouple placed near the bottom of the reactor. The instrumental uncertainties in temperature and pressure were within $\pm$ 0.1 K and $\pm$ 0.1 bar, respectively.

For chemical sorbents, a regeneration process was carried out for 1 hour under atmospheric pressure by increasing the temperature (93 ºC). Physical sorbents regeneration was achieved by simple flushing with an inert gas (nitrogen). In both cases the regeneration was carried out under nitrogen flow with a flow rate of 143.3 ml/min.

2.2.2 Batch reactor

For the absorbents with a tendency to dramatically increase viscosity upon saturation with CO_2 batch reactors were utilized in order to evaluate their CO_2 capturing ability. For the screening purposes, a tailor-made experimental setup with an inner diameter of 10 mm was designed, operating at atmospheric pressure (Fig.7).
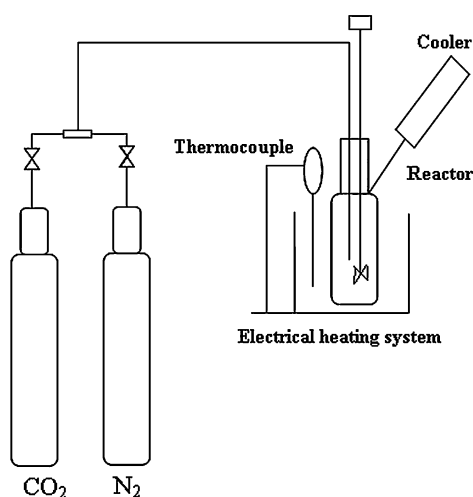
Figure 7. Batch reactor utilized in CO_2 uptake-release experiments.

In order to remove pre-dissolved impurities and captured atmospheric CO_2, flushing with an inert gas for 15 min was applied prior to experiments. The carbon dioxide flow was controlled by the flowmeter FlowPlot V 4.58 provided by Bronkhorst High-Tech B.V. (24.53 ml/min). In order to facilitate an efficient contact of CO_2 with the solution, a magnetic stirring system Heidolph MR 1000 was used with the stirring rate of 400 r.p.m. CO_2 absorption was performed at room temperature (22 ˚C). The temperature of the sample was kept constant by means of an external thermostat (Frigomix U provided by B. Braun Biotech International) filled with water.

In order to evaluate the effect of the mass transfer limitations, a batch reactor with a bigger volume (150 ml) equipped with an efficient mechanical stirring (300 r.p.m) was utilized. An electrical heater provided by Barnstead was applied instead of a water or oil bath to keep the temperature constant. In order to avoid evaporation losses, a cooler filled with glycol was installed.

2.2.3 TGA as a reactor

A thermogravimetric analyzer (TGA) Cahn D - 200 was applied to measure CO_2 capturing capacity of poly(ionic liquids) with a small sample volume (25 - 50 mg). The sample was placed in a quartz cup and suspended in the thermogravimetric analyser. Prior to purging with CO_2 the sample was held at 40 ºC under argon stream (191 ml/min) to remove all the impurities until the sample weight stabilized (3 hours). Then the temperature was decreased to room temperature (25 ºC) under Ar stream to avoid any gaseous impurities. For CO_2 adsorption studies the sample was held under CO_2 stream with a flow rate of 231 ml/min until saturation and the constant weight. Desorption of ionic (ILs) and poly(ionic liquid)s (PILs) was carried out under Ar stream at 40 ºC for 3 hours and 1 hour, respectively.

2.3 Analysis and product characterization

2.3.1 Level of CO_2 capture

The outlet gas stream from *the loop reactor* was led to a gas analyser (Geotech GA 2000/GA 2000 Plus Gas Analyser with a precision of ± 0.1 vol %). The gas analyzer was calibrated with all gases used in the experiment with known gas concentrations. The total

flow to the reactor was 260 ml/min. The outlet signal of the analyzer was transformed into molar flow at the ambient temperature (21 ºC). Upon integration the experimental values of CO_2 loading were calculated, based on the difference between the CH_4 and CO_2 responses **(II)**. To consider methane as an inert gas in the calculations, the following corrections were implemented:

$$\theta_{CO_2,a} = \theta_{CO_2,\exp} + \theta_{CH_4,a}, \tag{1}$$

where $\theta_{CO_2,\exp}$ represents the experimentally obtained CO_2 solubility in a particular solvent,

$\theta_{CH_4,a}$ corresponds to the CH_4 solubility in the same solvent.

In the case of CO_2 capture in the batch and the TGA reactors, the increment of weight was monitored as a function of time, until the saturation was achieved and equilibrium was established.

2.3.2 Viscosity and pH measurements

Viscosity of the absorbents mixtures before and after CO_2 absorption was measured on modular compact rheometer Anton Paar Physica MCK 300 at the shear rate 393 s^{-1}.

Solutions pH was measured with a pH meter (Mettler Toledo, S20 SevenEasy^{TM} pH).

2.3.3 Poly(ionic liquid)s
2.3.3.1 Scanning electron microscopy

The morphology and surface texture of the poly(ionic liquid)s were investigated by means of scanning electron microscopy (SEM). The analysis was performed by a Cambridge Instruments Stereoscan 360 with a ThermoNORAN Vantage X-ray detector as well as a LEO Gemini 1530 with a Thermo Scientific UltraDry Silicon Drift Detector (SDD).

2.3.3.2 Thermogravimetric analysis (TGA)

The degradation temperature for each poly(ionic liquid) was determined by means Cahn D -200 thermogravimetric analyzer.

2.3.3.3 Differential scanning calorimetry

The differential scanning calorimetric (DSC) curves were measured with a Mettler Toledo 822-instrument under nitrogen atmosphere. The samples were first heated from 25 °C to 150 °C with a heating rate of 10 °C/min. The samples were then kept at 150 °C for 10 minutes and cooled to -20 °C with a cooling rate of 10 °C/min, equilibrating them again for 10 minutes at -20 °C. Finally, the samples were heated from -20 °C to 150 °C, at 10 °C/min. The reported values of glass transition are from the final heating run.

2.3.4 Biogas sampling and analysis

Gas samples were withdrawn from the raw biogas and after upgrading with different absorbents in order to evaluate the level of removal of such contaminants as CO_2 and different volatile organic compounds (VOCs). The study of VOCs removal was performed under atmospheric pressure and at 27 °C.

The product biogas samples were collected in Nalophan $^®$ NA bags during a time-frame of 20 minutes. The sampling tubes were preconditioned for 8 hours at 300 ˚C under nitrogen stream. The gas samples were drawn into the sampling tubes with the adsorption material Tenax GR (2, 6-diphenylene-oxide polymer resin plus 30% graphite) by means of a Gilian Low Flow Air Sampling Pump LFS-113DC (Sensidyne, LP) with a sampling rate of 210 ml/min. The sample volume was in the range of 0.3 - 0.6 l, while for raw biogas sampling, a minimum volume of 0.3 l was used. The tubes were capped and stored at -18 ˚C until analyzed. Thermal desorption gas chromatograph-mass spectrometry (Tekmar Purge & Trap concentrator 3000/Agilent 6890+/5973 N MSD) was applied to extract the absorbed VOCs from the Tenax and analyze them as described **(II, VI)**. In the gas chromatography (GC) analysis, an Agilent Technologies HP5 capillary column was applied in all of the analyses (column characteristics: film 1 μm, diameter 0.25 mm, length 30 m). During desorption (at 250 ˚C for 10 min.), compounds were carried into the cryogenic trap where the temperature was kept at -120 ˚C. After desorption, the temperature of the cryogenic trap was ramped up to 250 ˚C. The initial GC oven temperature was 40 ˚C for 2 min, then ramped at 5 ˚C/min up to 150 ˚C, followed by a steeper ramp of 15 ˚C/min up to 250 ˚C and held constant at this temperature for 5 min. Helium with the flow rate 1.1 ml/min was used as the carrier gas.
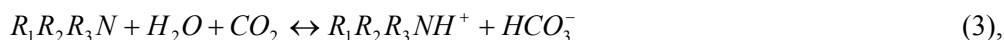
3. RESULTS AND DISCUSSIONS

3.3 Experiments with a model mixture of biogas

In the preliminary part of the work, various solvents claimed from the open literature to be effective in terms of CO_2 capture were investigated. Instead of real biogas, a model mixture consisting of CO_2 and CH_4 with 20 vol % of each gas was applied in these experiments. Nitrogen was applied as a carrier gas.

3.3.1 Amine solutions

Owing to their high capacity, amine scrubbing remains the most commonly used technology for removal of acid gas impurities [31].

Due to the different electronegativity of the atoms in the molecule, carbon dioxide possesses the properties of Lewis acid and can easily react with water and amines, which represent 'hard' Lewis bases. Thus, amine scrubbing process belongs to chemical solvent scrubbing. After binding with CO_2 there is formation of the carbamate (2) in case of primary and secondary amines and bicarbonate (3) for tertiary amines.

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH_2^+ + R_1R_2COO^- \tag{2}$$

$$R_1R_2R_3N + H_2O + CO_2 \leftrightarrow R_1R_2R_3NH^+ + HCO_3^- \tag{3},$$

where R represents an alkyl group or H atom.

An equation (3) usually includes additional protic species (e.g. alcohol) to facilitate the reaction of the thertiary amine.

In the present work, aqueous 15 wt % solutions of monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA) and amino-2-propanol (AMP) have been investigated representing primary, secondary, tertiary and sterically hindered solvents, respectively. Moreover, aqueous solutions of 15 wt % MDEA with an addition of different amounts of PZ were tested.

It was confirmed that the solutions with higher concentration of MEA exhibited higher CO_2 capturing efficiency since CO_2 absorption is proportional to the equilibrium

constant and the amine concentration. However, to avoid equipment corrosion, 15 wt % amine solutions were chosen for the subsequent work.

The results revealed that the efficiency in terms of CO_2 capture increased as follows: water < MDEA < DEA < AMP < MDEA + (2-5) wt % PZ < MEA **(II, III)**. The addition of PZ affects the process flexibility, providing the advantages of chemical and physical solvents. The CO_2 loading increases by increasing the percentage of PZ, but less than 15 wt % of PZ has to be used to avoid precipitation. At atmospheric pressure the mixture, containing 15 wt % of MDEA and 14 wt % of PZ (68 L CO_2 / L solution), outperformed 15 wt % MEA (50 L CO_2 / L solution) and the performance of 15 wt % MDEA (32 L CO_2 / L solution) solution by two-fold.

The experimental results demonstrated that the addition of 5 wt % of PZ increased the efficiency of abovementioned solutions by 24 - 50 vol %, the effect being the most significant in the case of MDEA solution **(II)**.

Isothermal absorption curves were determined confirming that equilibrium constants tend to decrease with a temperature rise. Increasing the temperature in general inhibits the dissolving reactions.

The pH dependence upon increasing pressure demonstrated that a higher pressure results in stronger CO_2 absorption (Fig. 8).
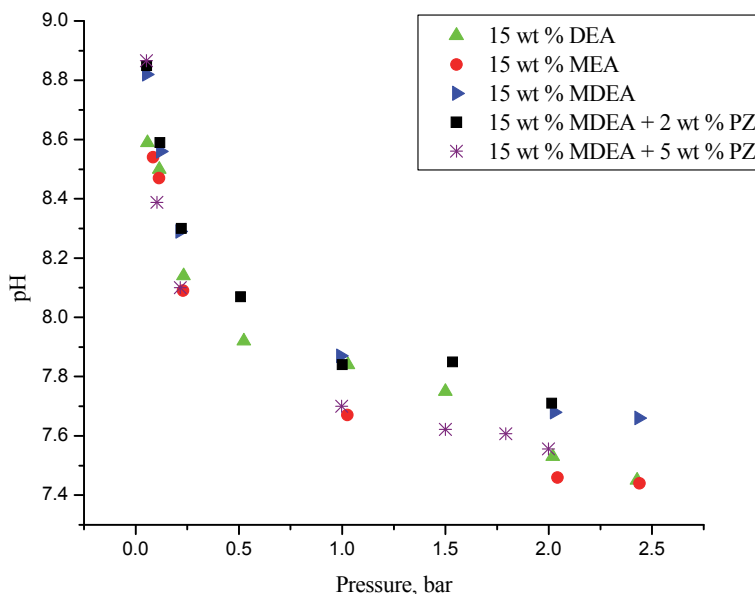

Figure 8. pH of the CO_2-treated aqueous amine solutions

The pressure dependence determined in coordinates $\theta = f(P_{CO_2})$ was rewritten by introducing the constants a_1 and a_2.

$$\theta = \frac{a_1 P_{CO_2}}{a_2 P_{CO_2} + 1} + \theta_{water} \, , \tag{4}$$

where a_1(bar^{-1}) and a_2 (bar^{-1}) are the constants, while the term θ_{water} describes the CO_2 loading of water, at particular pressure and temperature. The constants of equation for saturation type absorption isotherm tend to increase with an increase in the binding energy of absorption and with a decrease in temperature **(III)**.

A comparison between experimental and calculated values (eq. 4) revealed a certain discrepancy, especially notable in the case of 15 wt % MEA solution which might be associated with non-ideality of the solvent mixture (Fig. 9).
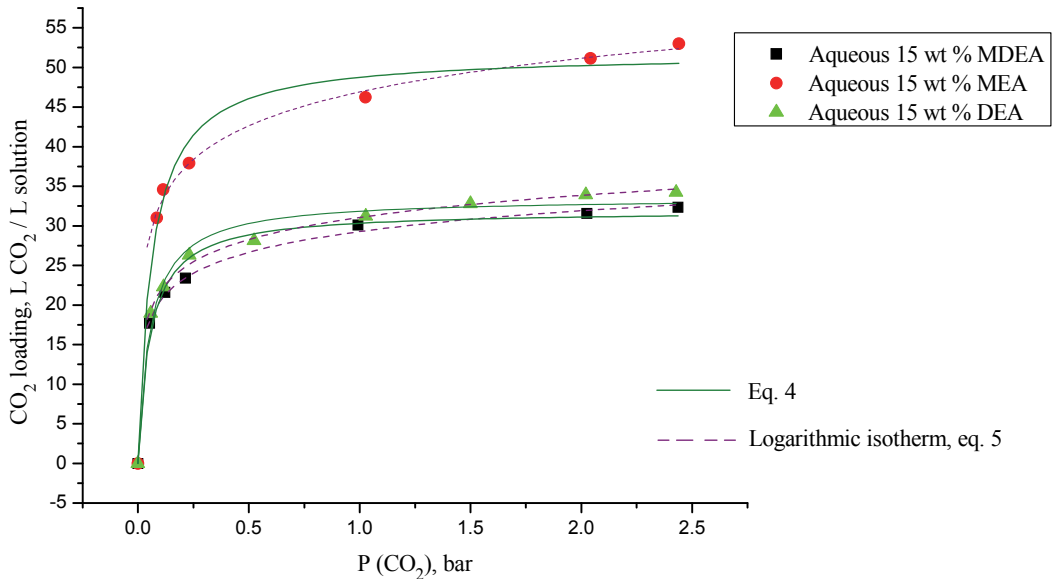
Figure 9. Pressure dependence and comparison between the experimental and calculated absorption curves for aqueous 15 wt % amine solutions at 20 ˚C.

Such non-ideal behavior can be well described by a logarithmic (or Temkin) absorption isotherm:

$$\theta = a_1 \ln a_2 P_{CO_2} + \theta_{water,} \tag{5}$$

where θ - CO_2 loading (L CO_2 / L solution),

a_1 – constant (L CO_2 / L solution),

a_2 – constant (bar^{-1}),

θ_{water} - CO_2 loading of water at particular pressure and temperature.

The logarithmic absorption value of a_1 corresponds to the CO_2 capturing efficiency of the amine solutions and is increasing in the following order: 15 wt % MEA > 15 wt % DEA > 15 wt % MDEA. The constant a_2 stands for the equilibrium constant corresponding to the maximum binding energy **(III)**.

The logarithmic approach represents a more simple way of analysing experimental data and was tested in the current work in the case of aqueous amine solutions (Fig. 10).
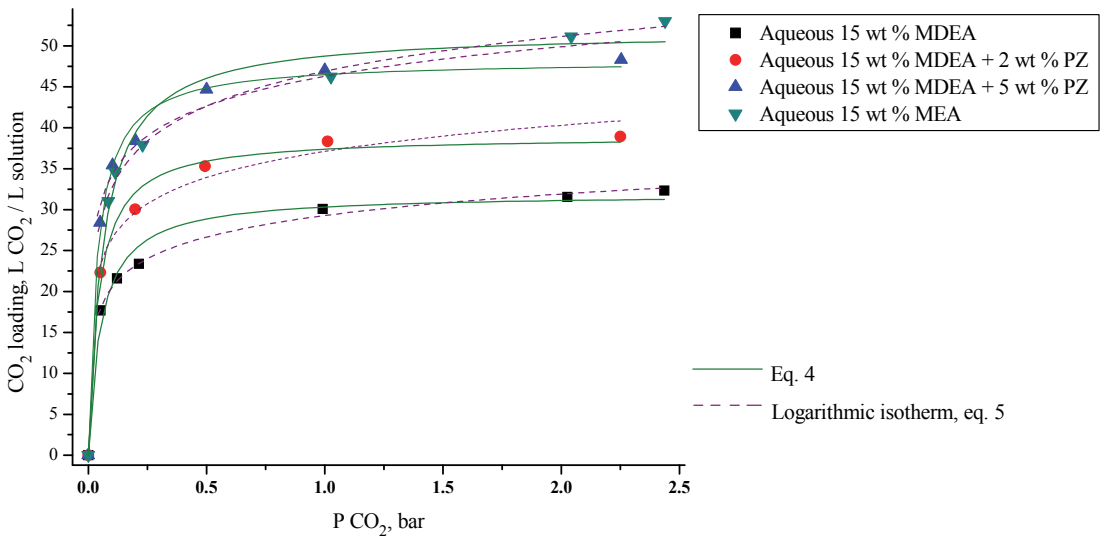
Figure 10. Comparison of suitability different equations to describe the experimental data obtained for aqueous amine solutions at 20 ˚C.

One of the hypotheses to explain such non-ideality was the assumption that the absorption equilibrium and the values of CO_2 loading depend not only on the amine concentration, but also on the amount of the protonated amine. However, from Fig. 8 it could be concluded that with increasing pressure more amine is protonated in the case of all amines used and cannot be a possible reason for the non-ideality, at least in the particular case of the MEA solution. Thus, a tentative hypothesis was proposed assuming that the ion-ion interactions influence the activity coefficients with altering CO_2 concentrations **(III)**.

As mentioned above, the addition of PZ enhanced the CO_2 capturing ability of amine solutions. Moreover, a quantitative analysis of absorption data was performed using an isotherm with saturation behaviour as well as a simple logarithmic model, accounting for the non-ideality of the mixtures (Fig. 10).

3.3.2 Ionic liquids

3.3.2.1 Traditional room-temperature ionic liquids

For the present study different ionic liquids were selected based on whether they belong to the class of chemical or physical solvents. Since for the physical ionic liquids the anion has a stronger effect on CO_2 solubility, several representatives of physical ionic liquids with different anions were studied such as 1-butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] and 1-butyl-3-methylimidazolium dicyanamide [C_4mim][DCA]. The CO_2 solubility increased in the following order: [DCA] < [BF_4] < [PF_6] **(II)** which corresponds well to the theory. Thus, an IL with fluor containing anion possesses higher CO_2 capturing efficiency than the one without a fluor group. Moreover, the efficiency increases with the number of fluor groups in the anion. However, in general, the efficiency of physical ionic liquids is quite low (< 4 L CO_2 / L solution) at low pressures and can be significantly increased at elevated pressure. Thus, an increase in the partial CO_2 pressure from 1 to 5 bars contributes to the rise in CO_2 capturing efficiency by a factor of 6, supporting a space-filling mechanism suggested by different research groups [32, 33].

1-butyl-3-methylimidazolium acetate [C$_4$mim][OAc] signifies the so called chemical ionic liquids since it absorbs CO_2 by means of the chemical reaction [19]. It was revealed to be efficient at low pressure and possessed the highest CO_2 removal efficiency (49 L CO_2 / L solution). As for amine solutions, in the case of ionic liquids the isothermal absorption curve confirmed the decline in CO_2 capturing efficiency upon rising temperature due to the decrease in equilibrium constants **(II)**.

In order to reduce the viscosity of ionic liquids and combine some of the existing advantages, mixtures of physical ionic liquids and chemical solvents were tested. This type of mixtures may offer additional advantages in terms of energy consumption and extend the range of pressures applied. Thereby, the application of the aqueous mixture consisting of 15 wt % [C$_4$mim][BF$_4$] ionic liquid and 15 wt % MDEA resulted in 14 times higher CO_2 capacity compared to the mixture without this amine. However, having investigated several mixtures, no extra additive capturing capability was observed and CO_2 loading was even lower than the theoretically expected one, calculated as a sum for individual sorbents, present in the mixture.

It should be noted that a minor synergetic effect was detected in the case of addition 5 wt % PZ to the aqueous 15 wt % [C$_4$mim][BF$_4$] mixture. The mixture displayed 3 vol. % higher capacity (22.36 L CO_2 / L solution) than the sum of capacities separately for the aqueous blended solution of 15 wt % [C$_4$mim][BF$_4$] (1.94 L CO_2 / L solution) and 5 wt % PZ (19.66 L CO_2 / L solution). This fact indicated a limited possibility of improving the absorption performance of physical ionic liquids at low pressures.

3.3.2.2 'Switchable' ionic liquids

In order to investigate the structure-activity relationship, various mixtures consisting of 1, 8 – diazabicyclo[5.4.0] undec-7-ene (DBU) and different (amino) alcohols were studied. 'Switchable' ionic liquids (SILs) were operated at low pressures since the CO_2 binding is based on the chemical reaction and they tend to behave as chemical solvents. After comparing the results obtained for SILs with the other solvents, it was concluded that the efficiency of SILs was at least two times higher than that of the chemical ionic liquid [C$_4$mim][OAc] and more than eight times better compared to the physical ionic liquid [C$_4$mim][BF$_4$] and the solution of pure DBU **(IV)**.

The results revealed that in case of SILs, the presence of an additional amino group in (amino) alcohol contributes to the enhanced CO_2 capturing capacity **(IV)**. Moreover, after comparing the mixtures based on 1-hexanol and 6-amino-1-hexanol, the conclusion was made that the presence of an amino group decreases the initial absorption rate. Furthermore, primary amines were more efficient than a secondary amine (L-prolinol) in CO_2 capture.

With the purpose of scaling up the experiments were repeated using two-fold amount of the solution (10 ml instead of 5 ml). The results are depicted in Figure 11.
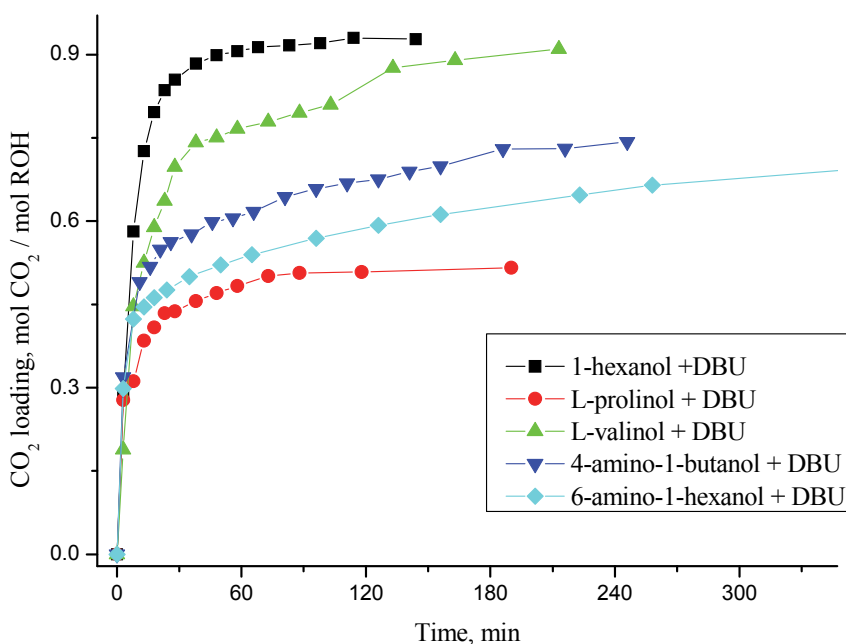

Figure 11. CO_2 capture by the SILs based on the equimolar mixture (1:1) of DBU and the different (amino) alcohols (V_L = 10 ml) at 22 ˚C and atmospheric pressure**.**

In general, all the regularities remained the same. However, in the case of the secondary amino alcohol L-prolinol, the CO_2 capturing capacity was lower (0. 5 mol CO_2 / mol ROH vs. 0.8 mol CO_2 / mol ROH). A steric effect and a charge –distribution in the heterocyclic amino ring of L-prolinol affected the CO_2 capturing efficiency and resulted in lower values compared to the studied primary amino alcohols. Moreover, the possible reasons for the differences in CO_2 uptake in a smaller and bigger absorbent volume could be variations in mass transfer, gas distribution and gas hold up, different residence time to

name a few. Furthermore, in case of bigger volume the time of the saturation with CO_2 for the mixtures of DBU with 4-amino-1-butanol and 6-amino-1-hexanol significantly increased. Thus, the time for the complete saturation of the DBU + 6-amino-1-hexanol mixture increased ten-folds and reaching 1100 minutes (0.85 mol CO_2 / mol ROH). As expected, due to limitations in gas distribution prevailing in the bigger volume the formation of carbamate in the solution proceeds slower than in the smaller volume. However, more research is needed to provide comprehensive conclusions.

CO_2 capture by SILs is concerned with the viscosity issues. Dramatic increase in the viscosity values upon CO_2 capture and crystal formation were observed upon CO_2 saturation (Fig. 12).
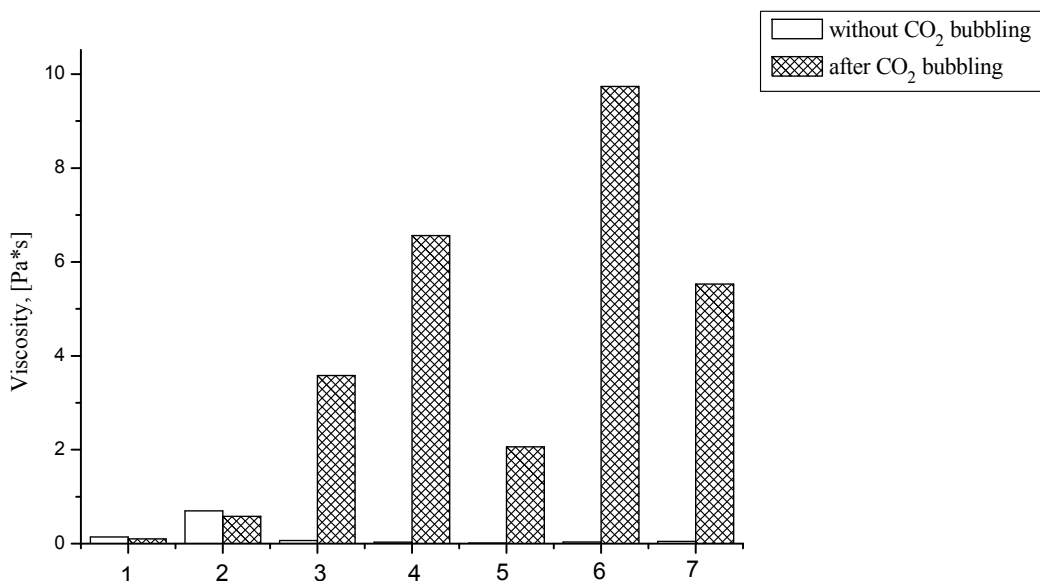
Figure 12. Viscosity increase upon CO_2 capture in ionic liquids [C_4mim][BF_4] (1) and [C_4mim][OAc] (2), and the switchable ionic liquid solutions based on mixture of DBU and L-prolinol (3), L-valinol (4), 1-hexanol (5), 4-amino-1-butanol (6) and 6-amino-1-hexanol (7).

For the SILs, the viscosity increased on average by a factor of six, while in the case of classical ILs the values even slightly decreased.

It was reported that a rise in the temperature provides an attractive decline in the viscosity **(IV)**. Moreover, the viscosity data confirmed that the ions inside the 'switchable' ionic liquids move less freely **(IV)**.

3.3.2.3 Poly(ionic liquid)s

In the present study several poly(ionic liquid)s (PILs) were investigated in terms of their CO_2 capturing capacity. The PILs consisted of poly(2-(1-butylimidazolium-3-yl)ethyl methacrylate [BIEMA] cation with different conter-anions, such as tetrafluoroborate [BF_4], hexafluorophospate [PF_6], bromide [Br], trifluoromethanesulfonate [TfO], bis(trifluoromethanesulfonyl)imide [NTf_2] and acetate [OAc] **(V)**.

Some of the studied PILs with monomers containing similar anions exhibited no sufficient advantages in CO_2 capturing efficiency (Fig. 13), except the PIL with Br-containing anion. However, P6 [BIEMA][Br] is difficult to work with due to its extremely high hygroscopic properties.
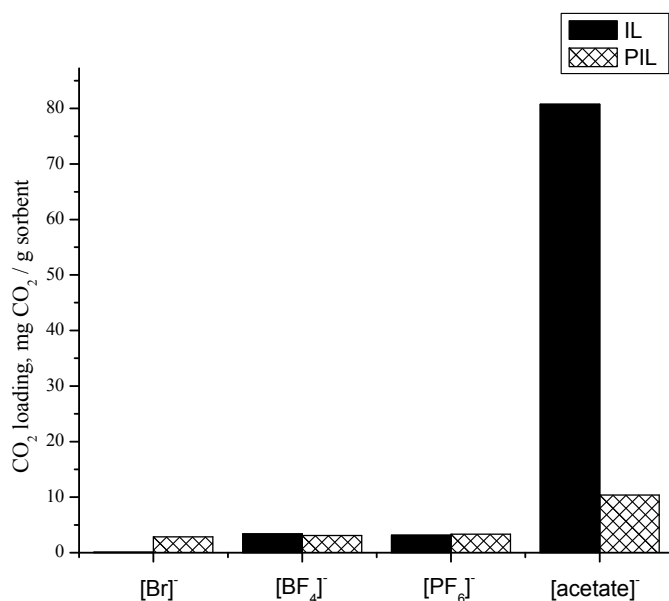
Figure 13. Comparison of ionic liquids and poly(ionic liquid)s containing similar anions.

The PILs with different counter-anions possessed different CO_2 capturing efficiency within the range 1.5 - 3.3 mg CO_2 / g PIL that corresponded to the following order: [NTf_2] < [TfO] < [Br] < [BF_4] < [PF_6]. It confirms the current understanding that

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in case of poly(ionic liquid)s fluorine atoms are not the key factor in enhancing CO_2 sorption. Moreover, bulky anions reduce the spare volume and impede CO_2 access to the polycation, responsible for CO_2 capture [21, 23].

In contrast to PILs with inorganic anions, PIL containing acetate anion exhibited higher CO_2 capturing capacity on average by a factor of 3 (12.5 mg CO_2 / g PIL). However, the absorption rate is much lower and it took more than 48 hours to reach the complete saturation with respect to CO_2, while for PILs with inorganic anions complete saturation was achieved within 20 minutes.

CO_2 capturing capacity slightly depends on the molecular weight of the polymer and the difference can be visible in case of Br-containing PILs.

Analysis of the surface texture revealed that the abovementioned PILs belong mostly to non-porous materials (Fig. 14) and did not show any visual changes after CO_2 capture/release.

P 5 [BIEMA][PF$_6$]   P 2 [BIEMA][BF$_4$]
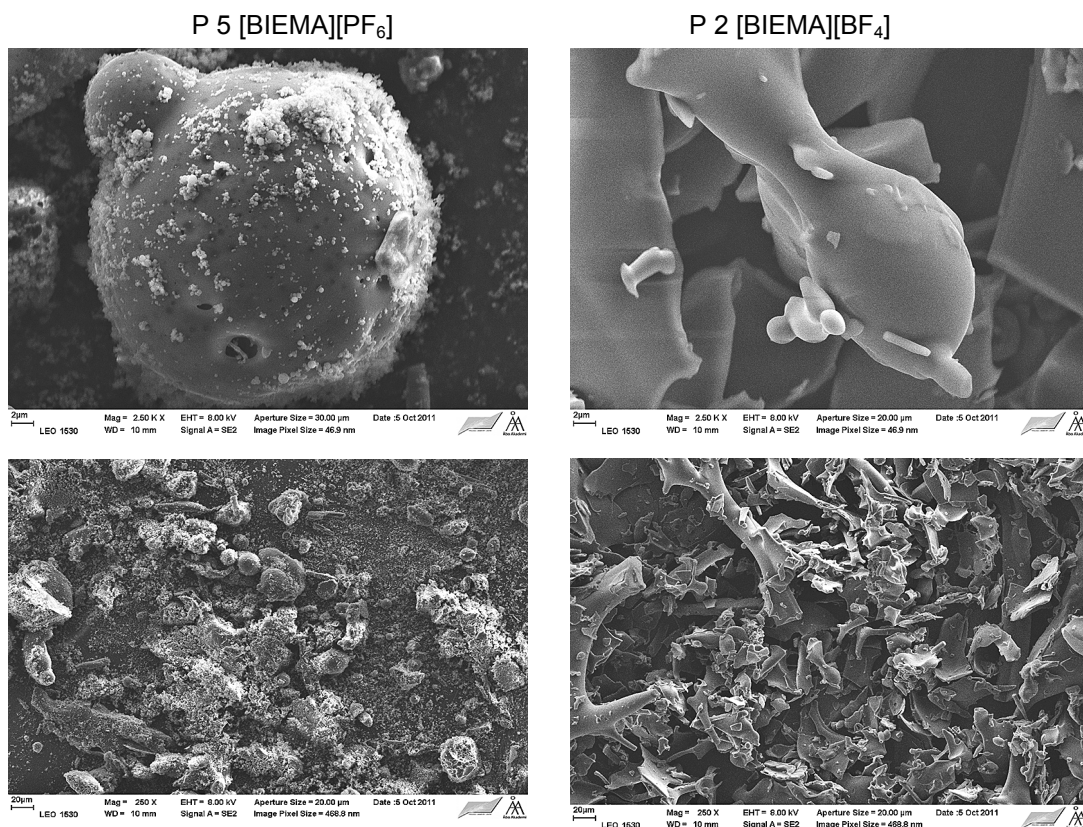
Figure 14. Scanning electron micrographs of fresh PILs with different counter-anions.

It was proved that an addition of a PIL into an IL does not increase the CO_2 capturing efficiency due to the viscosity increase and hampered diffusion of the gas **(V)**.

3.3.3 Amino acid salts

Since amino acid salts were claimed to be environmentally friendly sorbents with good CO_2 removal efficiency, a series of aqueous 15 wt % potassium salts of amino acid solutions, containing different functional groups such as hydroxyl (-OH), carbonyl (-CO-), carboxyl (-COOH-), as well as primary -NH$_2$ or secondary amino groups –NH were studied in the present work (Fig. 15).
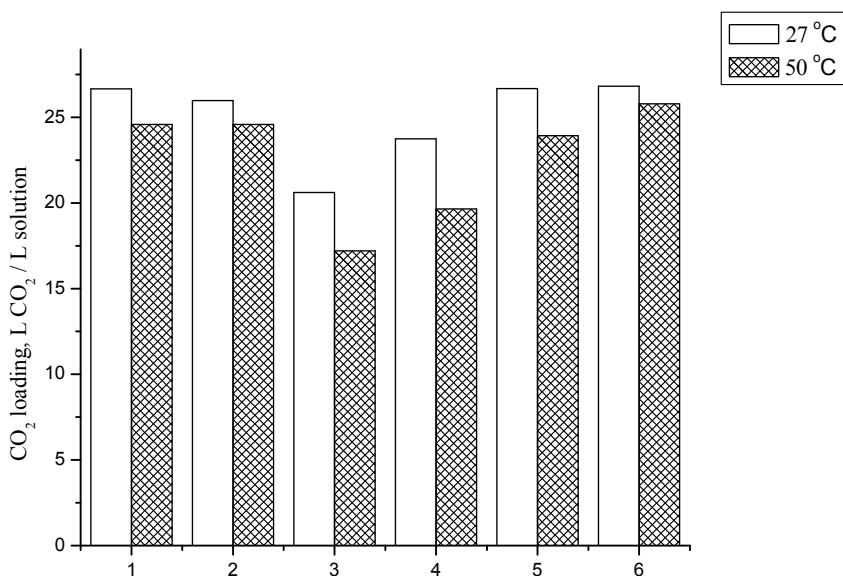
Figure 15. CO_2 capture in aqueous 15 wt % potassium salts of the following amino acids: [1] – L-alanine; [2]- beta-alanine; [3] – L-asparagine; [4] – DL – serine; [5] – glycine; [6] – sarcosine.

The best absorption performance was demonstrated by the sarcosine potassium salt (27 L CO_2 / L solution), being, however, inferior to the absorption performance of the

amine solutions (> 32 L CO_2 / L solution) and [C_4mim][OAc] ionic liquid (49 L CO_2 / L solution).

Moreover, the results revealed that the efficiency in terms of CO_2 capture was lower than in the case of the solution with equal amount of potassium hydroxide (28.4 L CO_2 /L solution). The formation of precipitate was observed after application of asparagine potassium salt; however, increased temperature diminished the solid precipitate formation.

The addition of 5 wt % PZ did not provide any synergy and the resulting capacity for aqueous solutions of amino acid salts as well as for amino acids was even less than the theoretically expected one.

3.3.4 Solvent regeneration and recyclability

All the applied sorbents were tested in terms of their regeneration since recyclability is a key factor of any scrubbing process. Solvent regeneration is a substantial and complicated field and requires rigorous studies to be completed. In the present study, a preliminary screening was performed in order to have initial comparison and make conclusions for the forthcoming work.

Physical solvents confirmed their ability to be regenerated by simple flushing. Complete release of CO_2 was reached both for physical ILs and for physical PILs **(II, V)**.

The regeneration of a chemical solvent is more demanding since besides bubbling an inert gas, increased temperature is always required. The regeneration for most of the studied chemical sorbents was carried out under N_2 passing at 93 ˚C **(II)** for 1 hour, while for SILs several temperatures were tested (22 ˚C, 107 ˚C and degradation temperature) **(IV)**. In the case of PILs, the restrictive limit was dictated by the glass transition temperature of the polymers, since sample melting significantly affected the sorption characteristics **(V)**.

The results indicated that an aqueous 15 wt % MDEA solution possessed minimal decrease in the solvent efficiency (<3 vol %). Other amine solutions exhibited a reduction of their efficiency that might be caused by solvent degradation or uncomplete CO_2 release since the required temperature for CO_2 desorption is in the range of 110 - 130 ˚C [18].

The regeneration of [C_4mim][OAc] at the mentioned conditions revealed an efficiency loss of ca. 30 vol. % (33.7 L CO_2 / L solution). Here it should be mentioned that this IL evolves CO_2 at 79 °C [18] and the influence of insufficient temperature for CO_2 release should be eliminated. It was proven that in the case of smaller volume of the IL, the initial value of CO_2 capacity was achieved within one hour treatment since an efficient mixing was provided. [C_4mim][OAc] was thus proven to be a recyclable sorbent. When the loop reactor was entirely filled with the IL, increasing the treatment time (up to 4.5 hour) did not provide better regeneration and the capacity of the regenerated IL stayed in the range of 18 - 22 L CO_2 / L solution. This fact confirmed that besides increased temperature, rigorous mixing and bubbling with an inert gas are needed for the CO_2 release from the IL.

As mentioned above, in the case of SILs several temperatures were tried for the initial optimization of the release process **(IV)**. Some of the SILs can be considered as recyclable solvents. One striking example is the mixture of DBU and 1-hexanol (1:1) with CO_2 absorption/release performed at 22/ 107 °C and under atmospheric pressure.

Regeneration at degradation temperature was proven as the most suitable method for better CO_2 release and was applied for the regeneration process in the forthcoming work. While increasing the liquid volume of the samples, the experiments were repeated (Fig. 16) and dependencies similar to the ones reported in **(IV)** were confirmed.

The mixtures of an amidine with 1-hexanol (Fig. 17a) and 6-amino-1-hexanol were verified to be recyclable along with L-prolinol (Fig. 16).

However, the efficiency of DBU + L-prolinol mixture was significantly inferior to the abovementioned solutions and cannot be considered as a competitive alternative.

PILs with inorganic anions also demonstrated recyclable properties (Fig. 17b). Moreover, CO_2 can be released through flushing with an inert gas (Ar). The regeneration of the PIL with [OAc] anion appeared much more complicated in terms of time required and the complete release of CO_2 was difficult to achieve **(V)**.
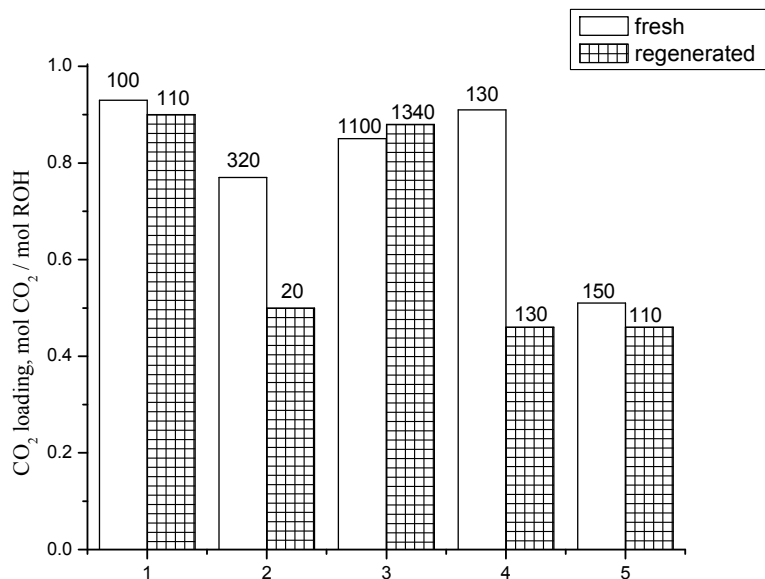
Figure 16. CO_2 sorption capacity of fresh and regenerated (at degradation temperature) 'switchable' solvents (V_L= 10 ml), based on the equimolar (1:1) mixture of DBU and the following (amino) alcohols: (1) - 1-hexanol, (2) – 4-amino-1-butanol, (3) – 6-amino-1-hexanol, (4) – L-valinol, (5) – L-prolinol. The numbers above show the duration of the saturation process.
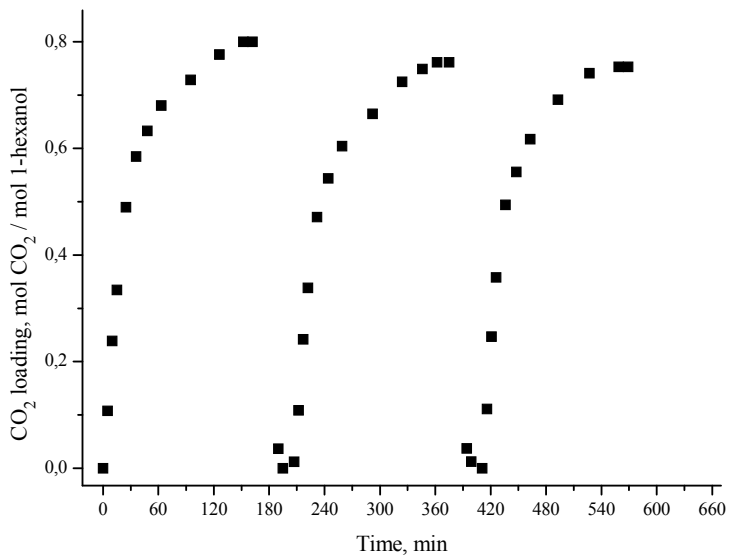
a)
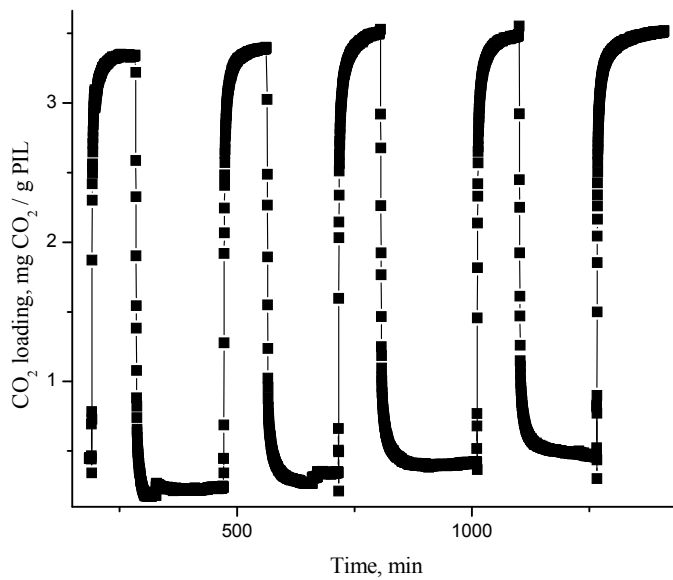
b)

Figure 17. Reversible properties of (a) SIL based on DBU and 1-hexanol mixture (1:1) and (b) PIL P6 [BIEMA] [BF$_4$].

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3.3.5 Comparison of different methods

As a result of the present study a comparison of the best options for CO_2 capture and biogas upgrading was done, which is summarized in Table 1.

Table 1. Comparison of the key properties for the selected, high-performance solvents at $P\ (CO_2) = 1$ bar

№	Solvent type	Solvent	CO_2 mole fraction	Viscosity at 25 ˚C before CO_2 uptake, cP	Regeneration mol % efficiency loss
1	Chemical	15 wt % MEA	0.038	1.14	42
2	Chemical	15 wt % MDEA	0.026	1.15	3
3	Chemical	15 wt % MDEA + 5 wt % PZ	0.038	-	16
4	Chemical IL	[C$_4$mim][acetate]	0.271	697	24
5	Physical IL	[C$_4$mim][BF$_4$]	0.018	141	0
6	Chemical PIL	PIL P7 [BIEMA] [OAc]	0.010[*]	-	
7	Physical PIL	PIL P6 [BIEMA] [BF$_4$]	0.004[*]	-	<2
8	SIL	DBU + 1-hexanol	0.317	9.43	5
9	SIL	DBU + 6-amino-1-hexanol	0.303	44.7	2

[*] mass fraction in case of poly(ionic liquid)s

The values presented were determined in the temperature range of 22 - 27 ˚C and the CO_2 partial pressure of 1 bar. In order to make a clear comparison, the calculations were made in mole fraction for liquid absorbents and mass fraction for solid sorbents such as poly (ionic liquid)s.

During the present study, amines were confirmed to be highly efficient in terms of CO_2 capture (entries 1-3). However, one can see that SILs and the chemical ionic liquid can become obvious alternatives (entries 8, 9 and 4). Moreover, the studied solvents demonstrated an elevated absorption performance in terms of CO_2 capture, compared to

water (mole fraction 0.0008). Increasing the partial pressure of CO_2 two-folds results in an efficiency increase by a factor of 4.5 (mole fraction 0.0035) which is still lower than for the organic solvents.

A pressure increase can also significantly affect the capacity of physical ILs. While at atmospheric pressure the value of mole fraction of CO_2 capture in the [C4mim][BF4] corresponded to 0.018 (entry 5), at 2 and 5 bar it was increased by a factor of 5.5 and 23, respectively.

Moreover, the absorption performance of physical ILs and the physical solvent (Selexol) was compared and no significant difference in the solvent behavior upon increasing pressure was observed, indicating a possibility of Selexol replacement with IL if there are economic incentives to make such substitution.

At the same time, in terms of costs and viscosity (1 cP), water seems to be the best option compared to the studied sorbents (Table 1). Moreover, as mentioned, the viscosity of SILs increases dramatically upon CO_2 saturation (Fig. 12) and a temperature increase is needed in order to mitigate the viscosity increase. From the regeneration point of view, physical solvents and some of the PILs attract most of the attention since no heating is required, while for the others regeneration seems still challenging.

At the same time, PILs with their CO_2 capturing efficiency in the range of 3 - 12 mg CO_2 / g PIL appeared to be significantly inferior compared to such typical adsorbents as an activated carbon (AC) (83 mg CO_2 / g AC) and zeolite 13X (206 mg CO_2 / g zeolite) tested at similar conditions [34]. The application of supported PILs on the mentioned supports could contribute to their increased efficiency and take an advantage of high CO_2 absorption rate and recyclability demonstrated by PILs.

To sum up, the present study provides some guidelines how to make a comparison between the different sorbents. However, to estimate the entire cost of replacement of currently used amine solutions with the suggested alternatives, detailed technically-economic analysis still has to be implemented taking into consideration all capital and maintenance costs, solvent capacity, operational conditions and energy requirements for the solvent regeneration, etc. Such attempt has been performed to compare MEA solutions with the process based on the utilization [C4mim][OAc] by Shiflett et al [18] and revealed that in case of an application of an ionic liquid as a scrubbing media, the

process investment and energy losses can be reduced by 11 and 16 %, respectively. Moreover, it will contribute to the reduction in equipment footprint by 12 %.

3.4 Experiments with the real biogas

3.4.1 Comparison of the real biogas with its model mixture

After the experiments with a model mixture of biogas, the experiments with a real biogas obtained from BIOvakka Oy were carried out. The content of the major compounds such as methane (63.7 ± 2 vol %) and carbon dioxide (36.8 ± 4.6 vol %) was at corresponding levels as reported in an earlier study [1, 35].

The presence of different trace compounds distinguishes real biogas from its model mixture. The experimental results revealed that due to bicarbonate formation, the pH of amine absorption media decreased with an increase in pressure. While in the case of a model mixture the decline was proportional to the pressure, for the real biogas a certain non-ideality was observed (Fig. 18).
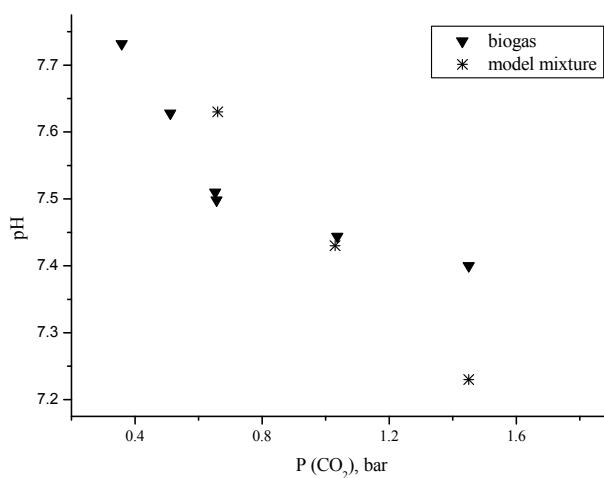
Figure 18. Comparison of pH values for a model mixture and the real biogas after upgrading with aqueous 15 wt % MDEA solution at 27 ˚C.

Moreover, the amount of CO_2 captured from the real biogas was always higher compared to the model mixture.

It was assumed that such non-ideality might be caused by the presence of trace compounds, contributing to the creation of an acidic environment and facilitating an improved CO_2 uptake (shifting absorption equilibrium).

3.4.2 Volatile organic compounds

The occurrence of volatile organic compounds (VOCs) was studied before and after biogas upgrading with different absorbents and particular attention was paid towards the sulphur- and silicon containing compounds, halogenated hydrocarbons and benzene-derivatives. Their presence usually originates from anaerobic degradation of bio-waste as well as from industrial waste coming to the wastewater treatment plants.

VOC trace contaminants have a detrimental effect on the engine performance and should be removed to improve the quality of biogas **(II, VI)**.

Based on the preliminary work, the following solutions were chosen for the upgrading purpose, namely, aqueous 15 wt % MEA, aqueous mixture of 15 wt % MDEA + 5 wt % PZ and the chemical IL [C_4mim][OAc].

The results revealed that the ionic liquid was superior not only in terms of CO_2 capture per se but also in terms of VOCs removal (Fig. 19). A detailed study is presented in paper **(VI)**.

After 20 minutes of upgrading, total concentration of the selected sulphur compounds, siloxanes and benzene-derivatives was diminished by 70 wt %, 65 wt % and 80 wt %, respectively. Selective extraction of the compounds containing aromatic moieties is usually associated with the π-π interactions between the imidazolium ring of the IL and an aromatic ring of a contaminant.

The best efficiency in terms of the siloxane removal was achieved by the aqueous (15 wt % MDEA + 5 wt % PZ) solvent mixture due to the strong basic properties contributing to the cleavage of Si-O bonds. As the main result, a 4.5 times decrease in the D4 siloxane mass concentration was detected.
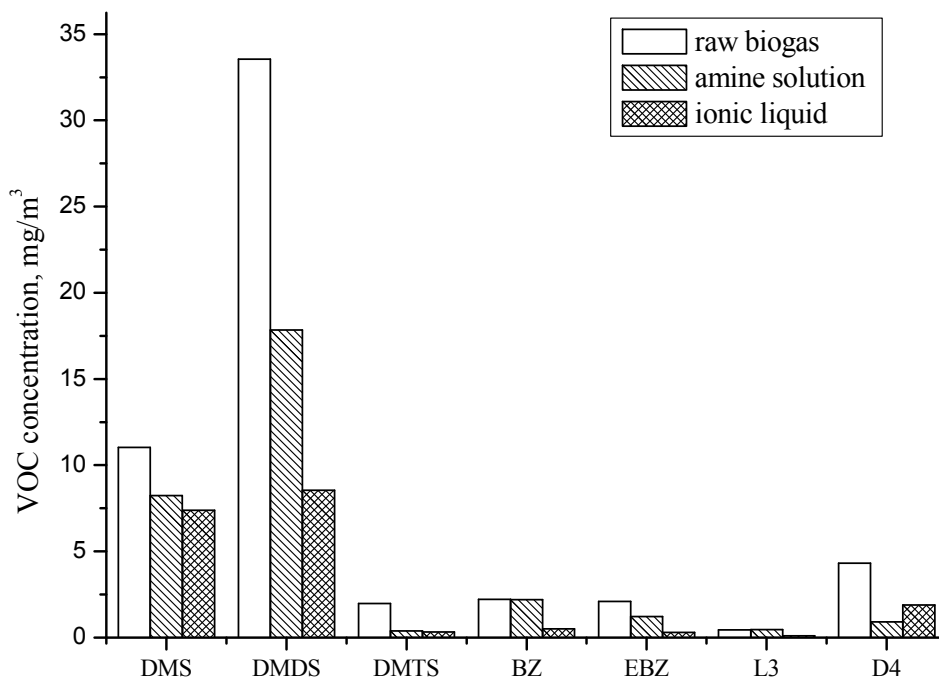
Figure 19. The occurence of the selected VOCs in raw biogas before and after upgrading with ionic liquid [C₄mim][OAc] and aqueous amine solution (15 wt % MDEA + 5 wt % PZ), where DMS - dimethyl sulfide, DMDS - dimethyl disulfide, DMTS - dimethyl trisulfide, BZ - benzene, EBZ - ethyl benzene, L3 – octamethyltrisiloxane, D4 – octamethylcyclotetrasiloxane.

However, in the open literature different processes with higher removal efficiency have been reported. Thus, the application of pressurazed water and the activated carbon, coated with potassium hydroxide was claimed to result in ca. 90 wt % VOSCs removal in the exhaust gas. Silica gel demonstrated the capacity for siloxanes of 100 mg/g, while in case of the studied solvents is was significantly lower (0.03 μg siloxanes / g IL and 0.02 μg siloxanes / g amine solution). This means that the optimization of the upgrading procedure and the rigorous choice of the ionic liquids are still needed in order to make the process a true alternative to the currently applied absorbents for biogas upgrading.

4. CONCLUSIONS

1. The most important research on CO_2 separation as a part of biogas upgrading which was reported in the literature was summarized and compared. Particular attention was paid towards amine solutions as the most commonly used technologies and emerging 'green' solvents such as ionic liquids.

2. Within the scope of the current work, a realistic comparison of various categories of solvents was performed in terms of CO_2 capture from a model biogas mixture. It was revealed that the studied amine solutions along with the chemical ionic liquid [C_4mim][OAc] possessed higher CO_2 loading capacity than the other studied compounds. Moreover, an addition of piperazine brings along extra benefits in terms of CO_2 removal in average by 30 vol %. Furthermore, the study revealed that the 'switchable' ionic liquid mixture consisting of DBU and 1-hexanol exhibited prominent CO_2 removal efficiency and reversible sorption characteristics.

3. A quantitative analysis of the absorption data obtained for amine solutions was performed using saturation-type and simple logarithmic models. As a result, the non-ideality in the sorption behavior of the aqueous MEA mixture was confirmed and evaluated.

4. The study confirmed different regeneration requirements for chemical and physical solvents. Regeneration of chemical solvents appeared to be challenging since the efficiency loss in some cases reached 30 - 40 vol %.

5. It was determined that the dramatic viscosity increase upon CO_2 saturation belongs to the main drawback of 'switchable' ionic liquids (SILs). However, the viscosity declines steadily upon temperature increase. The effect was the most prominent in the case of the mixture comprising of CO_2, DBU and 4-amino-1-butanol. Moreover, the present study demonstrated that CO_2 absorption performance was influenced by the structure of the (amino) alcohols applied.

6. It was demonstrated that not all poly(ionic liquid)s exhibit advanced CO_2 capturing properties compared to the ionic liquids with the same counter-anion. In the present study, poly(ionic liquid) with the [BIEMA] cation did not facilitate extended CO_2 adsorption. However, as expected, the sorption rate in case of poly(ionic liquid)s was much higher compared to the 'classical' ionic liquids.

7. The difference in the composition of biogas via mesophilic and thermophilic process was demonstrated. The experiments for upgrading real biogas samples were performed. New light was shed on ionic liquids as separation media with respect to VOCs removal. The occurrence of trace compounds in the treated biogas was significantly affected by the applied solvents. Thus, an alternative method for biogas upgrading can be developed to provide better biogas utilization.

NOTATIONS

θ_{CO_2} - CO$_2$ loading

η - viscosity

MEA - monoethanolamine
MDEA - N-methyldiethanolamine
AMP - amino- 2- propanol
DEA - diethanolamine
PZ - piperazine
DBU – 1, 8-diazabicyclo[5.4.0] undec-7-ene
DBN – 1, 5-diazabicyclo(4.3.0)non-5-ene
[C$_4$mim][BF$_4$] - 1-butyl-3-methylimidazolium tetrafluoroborate
[C$_4$mim][PF$_6$] - 1-butyl-3-methylimidazolium hexafluorophosphate
[C$_4$mim][DCA] - 1-butyl-3-methylimidazolium dicyanamide
[C$_4$mim][Br] - 1-butyl-3-methylimidazolium bromide
[C$_4$mim][TfO] - 1-butyl-3-methylimidazolium trifluoromethanesulfonate
[C$_4$mim][NTf$_2$] - 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
[C$_4$mim][OAc]- 1-butyl-3-methylimidazolium acetate
PEG - polyethylene glycol 400 dimethyl ether
IL – ionic liquid
SIL – 'switchable' ionic liquid
PIL – poly(ionic liquid)
PIL [BIEMA] [BF$_4$] - poly(2-(1-butylimidazolium-3-yl)ethyl methacrylate tetrafluoroborate
VOCs – volatile organic compounds
DMS – dimethyl sulfide
DMDS – dimethyl disulfide
DMTS – dimethyl trisulfide
BZ - benzene
EBZ – ethyl benzene
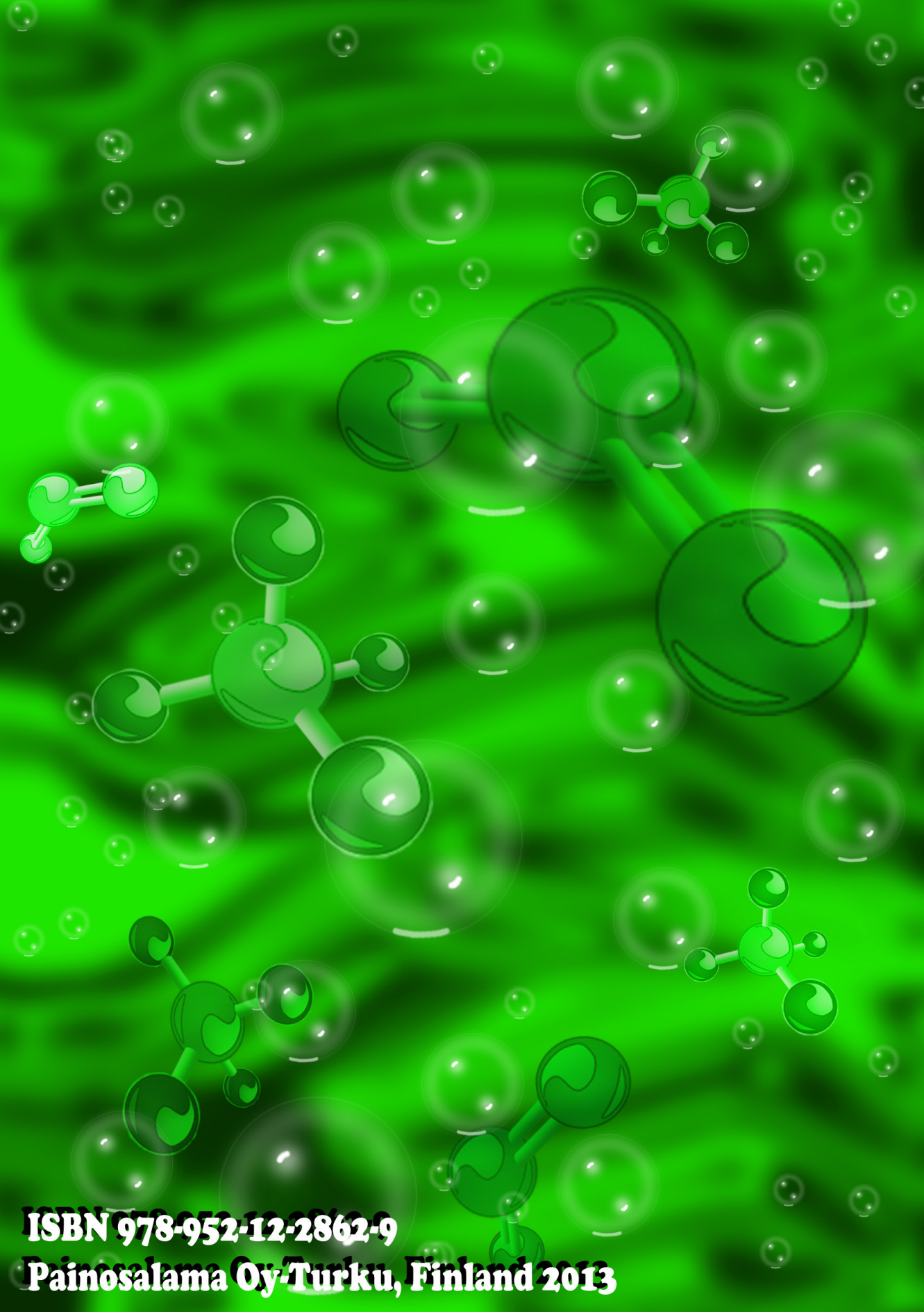L3 – octamethyltrisiloxane
D4 – octamethylcyclotetrasiloxane

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