Viability of Shale Gas and CO_2 Removal using 1-Butyl-3-Methylimidazolium Tetrafluoroborate

Syed Mohammad Bilal Kazmi[1], Dr Zahoor ul Hussain awan[2], Dr Saud hashmi[3]
Department of chemical engineering
N.E.D University of Engineering and technology
Karachi, Pakistan.

Abstract:- Worldwide strict rules are in place to control the greenhouse gas emissions. Ionic liquid are rapidly receiving the attention of the world in this regard as the most effective and potentially viable candidate for the capturing of the CO_2 and make the process environment friendly . The selection of ionic liquid from its broader class with the potential to remove the CO_2 is considered as a challenging task. Considering the selective removal of CO_2 [Bmim][BF4] has been selected as the potential solvent based on its selectivity and solubility of CO_2 and shale gas components. Furthermore, a suitable thermodynamic model has been adapted based on the physical and chemical data of the ionic liquid and incorporating it on the ASPEN Plus® process simulation software to evaluate the ionic liquid based decarbonization technology. The results shows that around 90% of CO_2 has been absorbed by the ionic liquid in comparison to the amine based solvent commercially been utilized for the process. Two processing model have been used single and multi-stage flashing after the absorption column.

Keywords:- *Shale gas, amines, ionic liquid, CO2 removal, energy efficient.*

I. INTRODUCTION

Shale makes up around 60% of the earth sedimentary rocks but types of shale differ from place to place. Shale is a sort of sedimentary rocks which generally comprises of laminated and fine grained sedimentary rocks composed of silt and clay sized particles. Shale gas is not the same as the traditional petroleum gas. Shale gas is found in the concentrated reservoirs and is caught in substantially smaller pockets throughout the shale rock. Shale gas is often found in the areas where mud, silt and other sediments are deposited. The main shale gas extraction was completed in the eighteenth century in Fredonia New York. The modern creation of the shale gas began not until 1970[2].

In 2013 division of energy in the United States led an investigation with the assistance of energy data organization (EIA) and recognized the capability of shale reserves in 41 unique nations. The report featured the geochemical attributes and furthermore recognized the measure of recoverable shale gas as appeared in figure 1[1]. In the report, it has been demonstrated that around approx 31000 trillion cubic feet (tcf) of shale saves are accessible of which actually recoverable shale gas is around 7000-8000 tcf [2].

The report also highlights that resources of the shale gas are majorly found in the North America, South America, Africa and Asian countries. In view of the Asian countries after china Pakistan is considered to be the state rich in shale oil and shale gas reserves with an estimated technically recoverable reserves of around 105 tcf of shale gas and 9 billion barrels of shale oil [1].

Shale gas has reformed the economy of the United States with its less reliance towards the oil imports and it has likewise affected their economy with the increase in work opportunity on the enormous scale [1].

Shale gas consists of methane as the main component and other light hydrocarbons as well. However before it can be utilized as a clean fuel it requires to be cleaned. Since the outflows of CO2 are the real issue in the atmosphere and consideration is given toward CO2 discharge control [20-21].

Decarbonization is the major technology used these days to control the emission with the help of solvents. The most common solvents used in the decarbonization are N-methyl pyrrolidone, poly ethylene glycol di methyl ether, methanol, sulfolane, di ethanolamine, mono ethanol amine and methyl di ethanol amine [9-12]. But generally these solvents have certain major drawbacks like high energy consumption during regeneration, insufficient capability to capture CO2, corrosion causing agent due to degradation of the amines[11][14][16].

To overcome these issues a new class of solvent has been studied widely known to be as “ionic liquids”. With their unique ability to work as an environmental friendly solvent [14-15].The Ionic liquid is generally termed as the “green solvents” [9-12].This name was given due to their unique ability both physically and chemically. Ionic liquids (ILs) are the heterocyclic compounds belong to the molten salt group and mostly they are composed of asymmetric and bulky cations (organic) and anions (organic/inorganic)[5][15][17-18][24-25].

The solubility of CO2 in ILs compared to other gases enables ionic liquids to separate CO2Even when there are low concentrations of CO2 in a mixed gas, the ionic liquid can be designed to incorporate [25]. They have the one of a kind property of non-flammability which makes them nonhazardous for the modern scale industries. For the most part, the vast majority of the ionic liquids show insignificant vapor pressure under normal process conditions in this manner they can be effortlessly be regenerated and prevent a significant loss to the environment which results in less contamination. A large portion of the ILS is thermally steady and chemically steady as well [4-7] .They have the solvation capacity with regards to organics and inorganic sorts of mixes.

In this work a possible solvent 1-butyl-3-methylimidazolium tetrafluoroborate has been utilized for screening CO2 from the shale gas as the potential solvent for the industrial scale decarbonization process using process simulation software ASPEN Plus®. Based on the suitable thermodynamic model and available parameters from the literature. Two process schemes are being considered and their results are being compared to the conventional process.

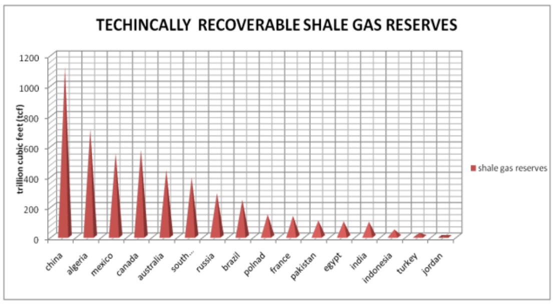

Fig 1:- Technically recoverable shale gas in different countries according to EIA report[1]

II. SELECTION

It is important to choose an ionic liquid having both high selectivity and solubility for the CO_2 and shale gas components[20]. Consequently to choose a suitable ionic liquid for the expulsion of CO_2 is a noteworthy step to be taken into account. Imidazolium based ionic liquid is chosen among the huge characterization of an ionic liquid because in this class of ionic liquid CO_2 is moderately more soluble generally because of the formation of strong hydrogen bond between the carbon atoms of imidazolium ring and the CO_2 atom [8].For the solubility of CO_2 in the ionic liquid a large amount of study has previously been done on the use of the imidazolium based ionic liquid with varying anions for e.g. $[BF4]^-$, $[Ntf2]^-$,$[PF6]^-$. The studies reveal that the solubility of CO_2 is high in ionic liquids having $–CF_3$ groups like $[BF4]^-$, $[Ntf2]^-$,$[PF6]^-$ [11]. This is generally due to fact that as the anion is highly fluorinated it results in more solubility of CO_2 in ionic liquid [25]. The other reason is availability of the substantial data of physical and chemical properties of both the cation i.e. 1-butyl-3-methylimidazolium and anion $[BF_4]^-$ because of the fact that ionic liquid gain it physical properties from the cation and chemical properties from the anion. Other factors which are vital in the selection of ionic liquid are the hydrophilic/hydrophobic behavior because it affects the solvation property of the ionic liquid. Thus based on the factors $[bmim][BF_4]$ is considered as the potential ionic liquid for this simulation study figure 2.

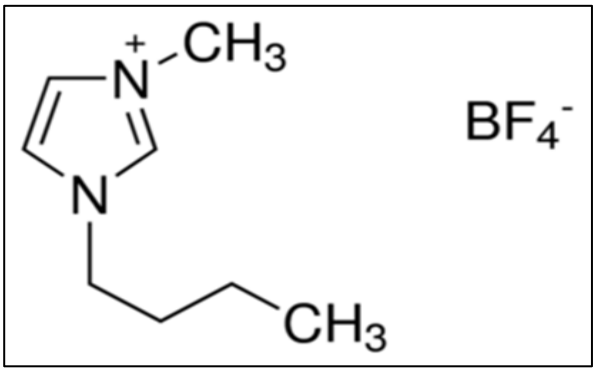

Fig 2:- Structural representation of $[bmim][BF_4]$

III. PROCESS SYNTHESIS

The main objective of the process is the expulsion of CO_2 from the shale gas utilizing ionic liquid. Routinely it is done with the assistance of amines. Feed gas components for the shale gas comprises of light hydrocarbons and an extensive level of methane gas. The typical composition of the various components of the hydrocarbons in shale gas found in Pakistan is portrayed in table 1.it is assumed that sulfur based impurities are removed in the desulfurization step. The process simulation is designed for the state of 32°C and since the shale gas is recovered from the well at high pressure so the model is simulated at 1000 psi**.**

Thermodynamic properties of the various ionic liquids and shale gas components involved in this study are predicted on the basis of NRTL (non-random two liquids)model. This model is used widely for the simulation of scrubbing process using amine. For ionic liquid the property prediction and equilibrium phase are modeled with the help of the data available at NIST data base for the ionic liquids [23].

Scalar properties incorporate the basic and volumetric properties of the gas and ionic liquids, the acentric factor, boiling point, etc which can be used in the prediction of the different thermodynamic properties and binary parameters. The basic properties of the ionic fluid are extracted from the literature. The temperature dependent properties are corresponded by the empirical equations where the coefficients and the scope of the experimental information are utilized. These properties are imperative as they help in the simulation model to help to break down the energy requests of the process.

Components	*Mol %*
Methane	67.72%
Ethane	6.57%
Propane	4%
Butane	0.52%
Pentane	0.19%
Co2	15%
N2	6%
Water	SATURATED

Table 1. Typical composition of shale gas in Pakistan

PROPERTY NAME	*unit*	*Value*
molecular weight	-	226.02518
critical temperature	C	359.15
critical pressure	Bar	20.4
critical volume	ml/mol	672
acentric factor	-	0.8489
normal boiling temperature	K	484.6

Table 2. Scalar properties of [Bmim][BF_4]

IV. PROCESS DESCRIPTION

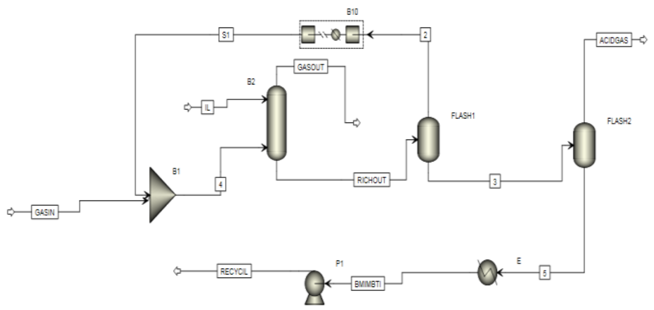

Fig 3:- Flow sheet of the two single stage process of Decarbonization

In this work, an outline procedure plot for the expulsion of CO_2 from the shale gas to meet the necessity of the decontaminated gas and regeneration of the ionic liquid is performed on the simulation platform of ASPEN plus®. Feed gas goes into the absorber column at 20°C and 68.95 bar. RadFrac is used to model the absorber column on ASPEN Plus; reaching in the absorber column it interacts counter currently with the ionic liquid. Rich dissolvable stream from the absorber flows into the column (flash column) at 20 bar which is utilized to reuse the lighter hydrocarbons once more into the process. The bottom of the main absorber column is additionally warmed to 27°C and enters into the second flash column at a decreased pressure of 1 bar. The bottom of the second flash column is also further additionally cooled to 25°C and reused back to the absorber column. The stream process model is shown in figure 3.

Another process scheme was also evaluated in this process model the feed enters the absorber column at 25°C and 68.95 bar. The bottom of the absorber column uses a series of the multistage columns to regenerate the solvent by reducing the pressure in each stage of the flash column. The schematic diagram of the process is shown in figure 4.

Also the ionic liquid processing is compared to the conventional process of the amine used for the decarbonization. In this process shale gas and its components enter into the refract column which is being used to model the absorber at 30°C and 60 bar pressure and counter currently interacts with the amine stream. The majority of gas laves the top of the column and rich stream containing (amines, CO_2 and traces of the gas) leaves the bottom of the absorber column. The rich stream goes into the flash column working at the reduce pressure of 14 bar it further separate out the remaining traces of the gas components and the CO_2 and amine leaves the bottom of the flash column. After the stream is preheated in the exchanger it goes into the regeneration column where amine is regenerated so it could again be used in the process fig 5.

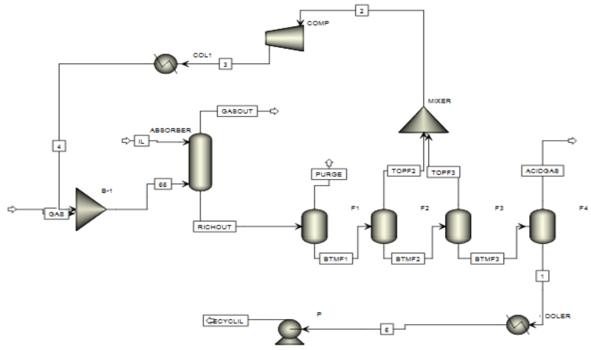

Fig 4:- Multistage flashing process for the Decarbonization using ionic liquid

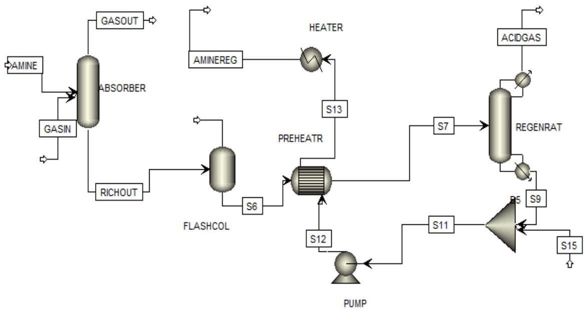

Fig 5:- Amine based process for the Decarbonization

V. RESULTS AND DISCUSSION

A. Effect of theoretical stages on co_2 removal:

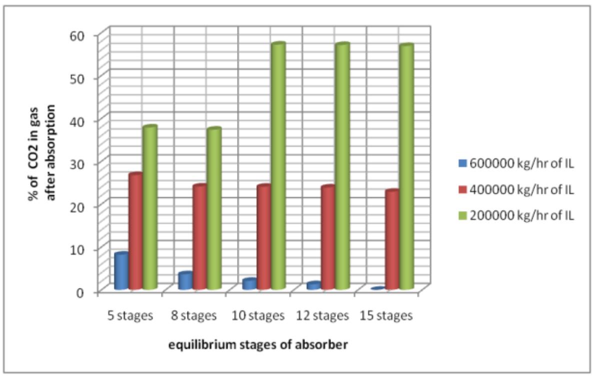

Fig 6:- Effect of ionic liquid on CO_2 removal at various equilibrium stages and at different mass flows

It is very apparent that as the number of equilibrium stages in the absorber column increases the separation of the CO_2 from the shale gas increases. The results for various stages and its separation performance are shown in Fig 6. It likewise depicts the performance of ionic fluid at various stream flows for the expulsion of CO_2 from the shale gas. The outcome demonstrates that 8-10 theoretical plates of the absorber are sensible to get the desired results.

The stream flow of ionic liquid is likewise critical and with the results of the simulation it additionally imperative to choose an appropriate measure of the flow stream of ionic liquid for the process to run at an optimal point. The simulation results demonstrate that ($4x10^5$ - $6x10^5$) kg/hr are the most reasonable mass stream of ionic liquid for the removal of the CO_2 from the shale gas stream. In the wake of setting the equilibrium stages to 10 at 30°C the impact of various mass streams of ionic liquids as shown in fig 7.

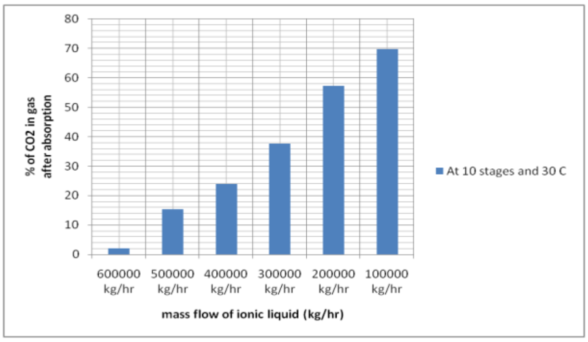

Fig 7:- % of CO_2 in gas after absorption at 10 stages at different mass flows

B. Regeneration column:

The purpose of the flash columns is for the regeneration of the ionic liquid [bmim][Bf_4] and furthermore the recovery of the remaining methane from the stream as well. To accomplish the two things you have to change the pressure of the flash column to recover the maximum measure of methane and maximum expulsion of CO_2 from the process. From the figure 8, we can see that by increasing the pressure the recovery of the methane falls marginally however, CO_2 recovery increases exponentially. It implies that there is a need to modify the pressure of the flash columns with the end goal that to achieve a high recuperation rate of CH_4 and maximum removal of CO_2 from the system. Hence the pressure of the flash column 1 is set at 20 bar , which brings about the recovery of around 74.20% of CO_2 from the feed gas stream and 75.59% of CH_4 recovery is accomplished.

The second flash column is working at the lower pressure of 1 bar to regenerate the ionic liquid [Bmim][bf_4] and remove the further amount acid gas from the system.

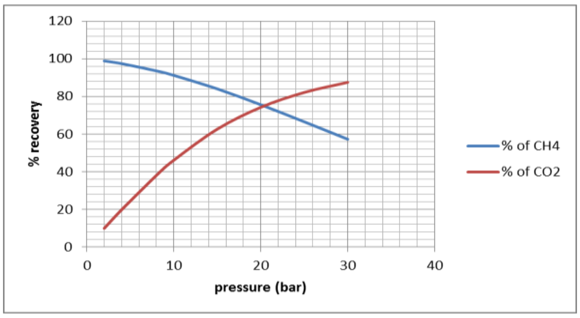

Fig 8:- % Recovery of CO_2 and CH_4 at various pressures of flash column

C. Solvent consumption

The amount of solvent is the key factor to be considered for both the process of amines and the process based on ionic liquid. The solvent consumption in ionic liquid based process is ($6x10^5$-$7x10^5$) kg/hr to recovery 90% methane. In contrast to the amine based process it requires lesser amount of amine as a solvent. On the other hand if the multi stage process is utilized using ionic liquid it almost requires 40 % less amount of ionic liquid [8].

The main advantage of using ionic liquid is generally because of its thermal stability, less corrosive in nature, negligible vapor pressure resulting in less volatility and generally less amount is lost and can be easily regenerated. These factors make ionic liquid a suitable replacement for the amines and would result in longer benefit.

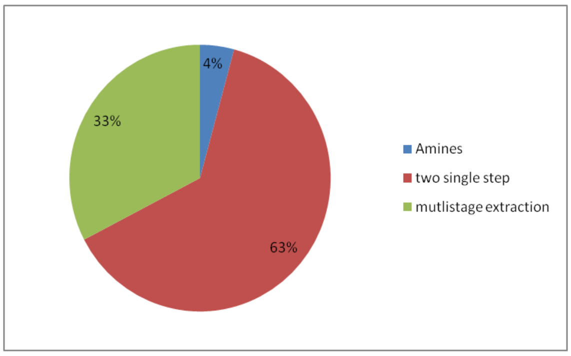

Fig 9:- Solvent demand of the various processes for the Decarbonization of shale gas

D. Energy analysis:

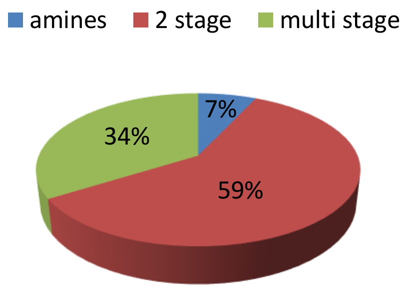

Fig 10:- Electricity consumption comparison between the processes

To consider the process and compare the difference between the two processing schemes energy consumption analysis is done both on the use of electricity and on the thermal energy consumption of the process. The results shows (fig.10.) that in comparison to the ionic liquid based processes amines based process requires less amount of electricity generally because in the ionic liquid process the lighter hydrocarbons are recovered using the flash column at low pressure and needs to be pressurized again to be recycled back into the process.

On the other if we compare the thermal analysis of both types of processing schemes one base on ionic liquid and other based on the amines we see that amine process requires a more thermal energy because of the reboiler in the regeneration section, where as in the ionic liquid based process the regeneration consists of the flash columns which requires small amount of heat at reduce pressure to achieve the regeneration process. If we consider the overall energy consumption as shown in fig, we see that amine based process consumes about (2576.12 KWe). Whereas ionic liquid based processes consumes around (2002.19 KWe) in the single stages process and (1213.1 KWe) in the multistage process (fig 11.).

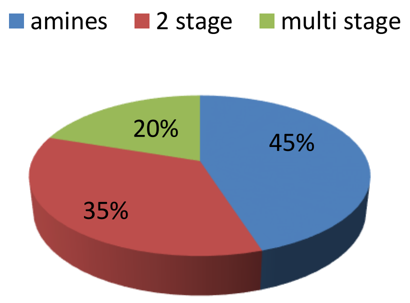

Fig 11:- Total thermal energy consumption comparison between the processes

E. Economic analysis

An economic analysis has also been performed based on the price of ionic liquid i.e. 1-butyl-3-methylimidazolium tetrafluoroborate. Generally speaking the price of the ionic liquid are somewhat much higher than the conventional solvent (amine).on comparing the laboratory scale amount (100gm) price of the [bmim][BF_4] is almost 6 times more than the methyldiethanolamine which is most popularly been used for the decarbonization of CO_2($180 vs. $30) However the ionic liquids are utilized in the small amount in contrast to the amine and they can be easily regenerated and reused in the multiple cycles. For example If 1-butyl-3-methylimidazolium tetrafluoroborate is being utilized for ten cycles without affecting its chemical properties then its use would become more affordable than the amine solvent. Therefore the convenience of the use of ionic liquids for industrial applications is linked to the possibility of recycling them without compromising their activities and their ability of separation without any Contamination [13].

VI. CONCLUSION

In this work the importance of shale gas keeping in view the energy demands and alternative fuels are considered. The process of decarbonization of the shale gas with the help of ionic liquid as solvent has been demonstrated. Two process schemes are being considered single stage absorption and multistage flashing. Both process results in the lower thermal energy consumption and effectively meets the requirements of the recovery of the methane as well as the lighter hydrocarbons.

NRTL thermodynamic model was used to model these processes on ASPEN plus.[Bmim][BF_4] was chosen as the ionic liquid solvent for the process. [Bmim][BF_4] was selected generally because a large amount of thermodynamic data required to in the simulation is available for it and it has high selectivity for the selective removal of CO_2 form the stream of hydrocarbons without dissolving greater amount of hydrocarbons in it. Multistage flashing was considered as the optimal process for the decarbonization in terms of energy consumption as well as the performance for the removal of CO_2 because the process can lead us to save around 30 % of the energy consumption.

Overall ionic liquid is proven to be a suitable replacement for the amines based process used commercially. The flexibility and inalienable advantages of ionic liquids in the procedure of CO_2 capture are giving rise to a promising field. Their potential as the physical absorbent is very alluring. The fact that amines for CO_2 removal have been produced through numerous years and that ILs are a new exploration field leaves space for further research and improvement.

REFERENCES

[1]. EIA/ARI World Shale Gas and Shale Oil Resource Assessment Technically Recoverable Shale Gas and Shale Oil Resources: An Assessment of 137 Shale Formations in 41 Countries outside the United States.

[2]. SDPI (sustainable policy development institute) draft report for shale oil and shale gas: lifeline for Pakistan.

[3]. Schlumberger report on “shale gas :a global resource” published in 2011.

[4]. Swapnil A. Dharaskar,Kailas L. Wasewara, Mahesh. N. Varmaa, Diwakar. Z Shendea, Chang KyooYoo Werner S, Haumann M, Wasserscheid P. Ionic liquids in chemical engineering. Annu Rev ChemBiomol 2010;1:203–30.

[5]. Ana R. Ferreira , Mara G. Freire , Jorge C. Ribeiro , Fernando M. Lopes , João G. Crespo , João A.P. Coutinho , Ionic liquids for thiols desulfurization: Experimental liquid–liquid equilibrium and COSMO-RS description http://dx.doi.org/10.1016/j.fuel.2014.03.020.

[6]. Borja Rodríguez-Cabo, Héctor Rodríguez, Eva Rodil, Alberto Arce, Ana SotoExtractive and oxidative-extractive desulfurization of fuels with ionic liquids Fuel 117 (2014) 882–889.

[7]. Xinyan Liu, Ying Huang, YongshengZhao,RafiqulGani, Xiangping Zhang, and Suojiang Zhang ionic liquid design and process simulation for decarbonization of shale gas DOI: 10.1021/acs.iecr.6b00029.

[8]. Amir HosseinJalili , Mohammad Shokouhi , Gerd Maurer , MasihHosseini-Jenab Solubility of CO_2 and H_2S in the ionic liquid1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate J. Chem. Thermodynamics 67 (2013) 55–62 http://dx.doi.org/10.1016/j.jct.2013.07.022

[9]. Santiago Aparicio and MertAtilhan Computational Study of Hexamethylguanidinium Lactate Ionic Liquid: A Candidate for Natural Gas Sweetening Energy Fuels 2010, 24, 4989–5001.

[10]. MohammadaliSafavi , Cyrus Ghotbi , VahidTaghikhani , Amir HosseinJalili , Ali Mehdizadeh Study of the solubility of CO_2, H_2S and their mixture in the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate: Experimental and modeling. J. Chem. Thermodynamics 65 (2013) 220–232
[11]. Ali Haghtalab, Alireza Afsharpour Solubility of CO2 + H2S gas mixture into different aqueous N-methyldiethanolamine solutions blended with 1-butyl-3-methyl imidazolium acetate ionic liquid Fluid Phase Equilibria 406 (2015) 10–20.
[12]. Andreani, L., Rocha, J.D., 2012. Use of ionic liquids in biodiesel production: a review.Braz. J. Chem. Eng. 29, 1e13.
[13]. Swapnil A. Dharaskar a, Kailas L. Wasewara,b,*, Mahesh N. Varma a, Diwakar Z. Shende a, ChangKyooYoo Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel Arabian Journal of Chemistry (2016) 9, 578–587.
[14]. Dharaskar, S., Wasewar, K., Varma, M., Shende, D., 2013a. Extractivedeep desulfurization of liquid fuels using Lewis based ionicliquids. J. Energy, 1–4.
[15]. Jiang, X., Nie, Y., Li, X., Wang, Z., 2008. Imidazolium based alkyl phosphate ionic liquids – A potential solvent for extractive desulfurization of fuel. Fuel 87 (1), 79–84.
[16]. Earle, M., Seddon, K., 2000. Ionic liquids, green solvents for the future. Pure Appl. Chem. 72, 1391–1398.
[17]. Zhou, Y., Antonietti, M., 2003. Synthesis of very small TiO2nanocrystals in a room-temperature ionic liquid and their self assembly toward mesoporous spherical aggregates. J. Am. Chem. Soc. 125, 14960–14961.
[18]. Mark B. Shiflett, David W. Drew, Robert A. Cantini,‡ and A. Yokozeki Carbon Dioxide Capture Using Ionic Liquid 1-Butyl-3-methylimidazolium Acetate Energy Fuels 2010, 24, 5781–5789.
[19]. Yingying Zhang a,b, XiaoyanJi a, YujiaoXie a, Xiaohua Lu b,Screening of conventional ionic liquids for carbon dioxide capture and separation Applied Energy 162 (2016) 1160–1170.
[20]. Mortazavi-Manesh S, Satyro MA, Marriott RA. Screening ionic liquids as candidates for separation of acid gases: solubility of hydrogen sulfide, methane, and ethane. AIChE J 2013; 59:2993–3005.
[21]. Jason E. Baraa,b, Christopher J. Gabrielb, Trevor K. Carlisle a, Dean E. Campera, Alexia Finotello a,Douglas L. Gina,b,, Richard D. Noblea, Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes Chemical Engineering Journal 147 (2009) 43–50.
[22]. NIST database for ionic liquid http://ilthermo.boulder.nist.gov/
[23]. FèlixLlovella,, Mariana B. Oliveirab, João A.P. Coutinho b, Lourdes F. Vegaa, Solubility of greenhouse and acid gases on the [C_4mim][MeSO4] ionic liquid for gas separation and CO_2 conversion Catalysis Today 255 (2015) 87–96.
[24]. Elena Torralba-Calleja, James Skinner, and David Gutiérrez-TausteCO2 Capture in Ionic Liquids: A Review of Solubilities and Experimental Methods Hindawi Publishing Corporation Journal of Chemistry Volume 2013, Article ID 473584.