

## Effect of Monoethanolamine Concentrations for CO<sub>2</sub> and H<sub>2</sub>S Elimination in Biogas Improving Process

Surajitr Pramuang

Faculty of Science and Technology, Loei Rajabhat University

234 Loei – Chiangkhan road, Muang Sub-District, Muang District, Loei Province, 42000 Thailand

**Corresponding Author:** [surajitr@lru.ac.th](mailto:surajitr@lru.ac.th)

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### Abstract

The utilization of raw biogas that low %CH<sub>4</sub> content with high %CO<sub>2</sub> and %H<sub>2</sub>S obtains low calorific value and metal corroded. The removal of CO<sub>2</sub> and H<sub>2</sub>S is needed in biogas improving process. The solution of MEA with different concentrations using for CO<sub>2</sub> and H<sub>2</sub>S elimination was investigated. A small biogas purifier consists of three parts of container with MEA solution volume 1.50 L, iron rust 1.20 kg and silica gel 1.50 kg using as the materials for chemical absorption and physical adsorption in purification process. The concentrations of MEA solution with 1, 1.50, 2, 2.50 and 3 mol L<sup>-1</sup> were compared the CO<sub>2</sub> and H<sub>2</sub>S removal performance and saturated duration. The raw biogas contains by averaged of 61.10% CH<sub>4</sub>, 37% CO<sub>2</sub>, 0.90% H<sub>2</sub>S, 0.30% O<sub>2</sub> and 0.70% others feeding through the biogas purifier with flowrate of 0.04 kg s<sup>-1</sup>. The output of CH<sub>4</sub> for MEA solution of 1, 1.50, 2, 2.50 and 3 mol.L<sup>-1</sup> were 91.30%, 91.80%, 92.10%, 90.40% and 92.50% respectively. The effect of high concentration obtained the high removal performance but the saturated duration was not different compare to the low concentration.

**Keywords:** Biogas purification, CO<sub>2</sub> removal, H<sub>2</sub>S removal, mono-ethanolamine

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### 1. Introduction

Biogas is produced from anaerobic degradation of organic materials by acetogens and methanogens bacteria. Raw biogas consists of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), moisture and trace gases such as oxygen, hydrogen ammonia and so on, by 45 – 60% CH<sub>4</sub>, 30 – 40% CO<sub>2</sub>, 1 – 5% O<sub>2</sub>, 0.10 – 1% H<sub>2</sub>S and trace gasses 0.10 – 2%. Methane is one of GHG when released to atmosphere with 28 times harmful power of CO<sub>2</sub>. The utilization of impurities biogas obtains low calorific value and damages device due to CO<sub>2</sub> is an incombustible gas, while H<sub>2</sub>S mixing with water to be sulfuric acid that is corroded metal. The removal of CO<sub>2</sub> and H<sub>2</sub>S is importance in the improving biogas with increasing CH<sub>4</sub> content above 96% for vehicle fuel [1]. The high purity methane is not only high calorific value but also high the knock resistance in internal combustion engine. Biogas upgrading methods are eliminated mixed gases from methane by physical, chemical and biological technologies due to its properties.

Mono ethanolamine (MEA) solution used for biogas purification in O.I. Maile, et al. [2 – 3] showed that CO<sub>2</sub> removal efficiency and absorption rate were high according to high concentration of MEA. According to Apichat Srichat, et al. [4] experiments using MEA solution with concentrations of 0.10 and 0.20 mol L<sup>-1</sup>, the flowrate of solution to biogas flowrate (L/G ratio) and solution concentration affected to CH<sub>4</sub> purifying. The higher L/G ratio obtained the higher yield of CH<sub>4</sub> concentration. The removal of CO<sub>2</sub> in biogas using MEA comparing to sodium hydroxide solution (NaOH) and aqueous

ammonia by Maizerwan Mel, et al. [5]. MEA solution was proven to be the good solvent by eliminating CO<sub>2</sub> less than 5% at the ambient condition. The CO<sub>2</sub> removal efficiency depended on temperature and concentration of absorption solvent.

The cost-effectiveness for biogas purification in a large scale is economically. The appropriate apparatus for biogas upgrading in farm scale or small scale is rare. This study attended the removal of CO<sub>2</sub> and H<sub>2</sub>S using different concentrations of MEA solution with a small apparatus for utilization to fan driving engine in an animal farm. The concentrations range from 1 to 3 mol.L<sup>-1</sup> were compared the removal efficiency and saturated duration.

## 2. Materials and Methods

### *Materials*

According to the characteristics of biogas as compound gases, the separation principle is based on different properties of CH<sub>4</sub> to CO<sub>2</sub>, H<sub>2</sub>S and others in fact of physical and chemical properties.

#### *The physical technology*

The pressure-swing adsorption (PSA) separates CO<sub>2</sub> and H<sub>2</sub>S by solid adsorption under high pressure environment. Because of CH<sub>4</sub> molecule is larger than CO<sub>2</sub> and H<sub>2</sub>S molecules, the mixture gases are adsorbed onto the porous adsorbents. The most commonly used adsorbents are zeolite, activated carbon, activated charcoal, silica gel and synthetic resins [6].

Cryogenic separation, this uses different temperatures to separate the mixture gases from CH<sub>4</sub>. The different melting points of CH<sub>4</sub> and mixture gases (CO<sub>2</sub> and H<sub>2</sub>S) by -182°C to -57°C for CO<sub>2</sub> and -82°C for H<sub>2</sub>S can be separated under cooled at elevated pressure condition. This technique obtains high purity biogas about 99% CH<sub>4</sub> but consumes high energy to operate.

Membrane separation, a microporous hydrophobic membrane is used as its selective permeability property. The gas-liquid separation that liquid absorbs CO<sub>2</sub> and H<sub>2</sub>S molecules flowing encounter direction through the membranes, while the gas-gas separation operates at high pressure. According to CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S and traced gases in biogas containing different sizes of gas molecules, the permeability through the membrane are different. The separation process is run in high pressure and high temperature conditions. This technique obtains 98% CH<sub>4</sub> purity at high pressure 20 – 40 bar and 92 – 97% CH<sub>4</sub> purify at lower pressure 8 – 10 bar [7].

Hydrate formation, the process works on the equilibrium of the gas components between gaseous phase and hydrate phase of CO<sub>2</sub>. The purity obtains CH<sub>4</sub> above 75% but the process consumes high energy and high CH<sub>4</sub> loss.

#### *The chemical technology*

Water soluble characteristics of CH<sub>4</sub> comparing to CO<sub>2</sub> and H<sub>2</sub>S is poor, so that CO<sub>2</sub> and H<sub>2</sub>S are separated. The water solubility of CH<sub>4</sub> is 26 times lower at 25°C than that of CO<sub>2</sub>. The method for separating mixture gases and CH<sub>4</sub> in chemical technology provides by chemical reactivity. Chemical absorption involves formation of reversible chemical bonds between the solute and the solvent.

Water scrubbing and organic scrubbing, the different solubility of biogas components is employed in principle. The absorbed biogas components are physically bound to the scrubbing liquid. The different binding force of non-polar molecule CH<sub>4</sub> and more polar molecule CO<sub>2</sub> and H<sub>2</sub>S can be separated in selective solvents. An organic solvent such as methanol can be employed in CO<sub>2</sub> removal while polyethylene glycol can be separated H<sub>2</sub>S due to its higher solubility in polyethylene glycol than CH<sub>4</sub> [6].

Chemical absorption, hydrocarbon compound with double bond such as CH<sub>4</sub> is non-polar molecule that is less reactivity with the polar solvents than that of CO<sub>2</sub> and H<sub>2</sub>S. The reaction sensitivity of CO<sub>2</sub> and H<sub>2</sub>S to amines solutions and alkali aqueous solutions is higher. So, amine solutions can be absorbed CO<sub>2</sub> and H<sub>2</sub>S separating from biogas obtaining purity over 90% CH<sub>4</sub> [2]. Chemical absorption of H<sub>2</sub>S using iron rust (iron oxide, Fe<sub>2</sub>O<sub>3</sub>) that reaction of H<sub>2</sub>S and Fe<sub>2</sub>O<sub>3</sub> forming Fe<sub>2</sub>S<sub>3</sub> by equation



Reaction of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  with MEA solution is complex expressing respectively in equations [8].



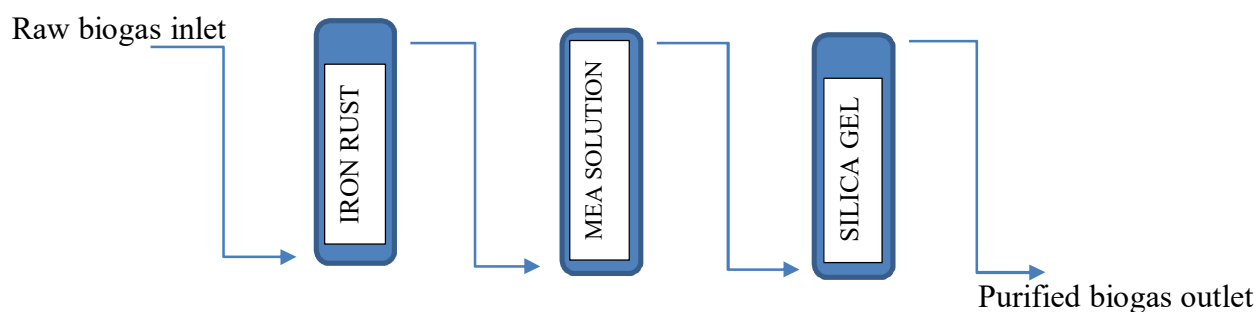
where R is an organic functional group namely ethanolic group,  $\text{HOC}_2\text{H}_4$  represented by  $\text{HO} - \text{CH}_2 - \text{CH}_2 -$ .

### *The biological technology*

The removal of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  by bacterial species takes place in specific conditions of oxygen lacking, pH and light. There are chemotrophic thiobacteria and phototrophic bacteria. Chemotrophic thiobacteria can purify  $\text{H}_2\text{S}$  in both aerobic and anaerobic conditions, while phototrophic bacteria provides in the presence of light and  $\text{CO}_2$ . Thiobacillus genus bacteria is well in a large scale for  $\text{H}_2\text{S}$  removal. The advantage of biological methods are low energy requirement, mild conditions and the elemental sulfur byproduct, but disadvantages with nutrients added for growing bacteria and needed small amount of  $\text{O}_2$  and  $\text{N}_2$ . The removal efficiency for  $\text{H}_2\text{S}$  depended on activity of bacteria obtaining over 80%  $\text{CH}_4$  purify in generally. This technology needs a large scale of biogas consumption due to the cost is high.

### *Method*

A small packed column of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  scrubbing using MEA solution, iron rust, and silica gel was used for the biogas improving process. Fig. 1 shows a diagram of biogas improving process respectively by  $\text{H}_2\text{S}$  elimination,  $\text{CO}_2$  elimination, and moisture adsorption. Raw biogas flows into the iron rust column for  $\text{H}_2\text{S}$  scrubbing and then passing through the MEA column for absorbing  $\text{CO}_2$ , finally moisture content will be adsorbed by silica gel column. The first two stages are chemical absorption technique and last one is physical adsorption technique. The packed column capacity contained an MEA solution for 1.50 L, iron rust 1.20 kg, and silica gel 1.50 kg (Fig. 2). The concentrations of MEA solution are 1, 1.50, 2.25, and 3  $\text{mol L}^{-1}$ . The raw biogas was obtained from the 50  $\text{m}^3$ -fixed dome reactor using pig's manure passing through the packed columns and then feeding to the engine-powered for the air blower of the evaporative conditioning system. The raw biogas was measured as mixed gases of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{O}_2$  at flow rate averaged of 0.04  $\text{kg s}^{-1}$  under real conditions of biogas utilization that it is high at the beginning and low at the end. The  $\text{CO}_2$  removal at different concentrations of the MEA solution was compared in the same amount of iron rust and silica gel.



**Fig. 1** Schematic of biogas improving by  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  eliminating and moisture adsorption



**Fig. 2** A small biogas purifier used for upgrading the engine fuel in the evaporative conditioning system

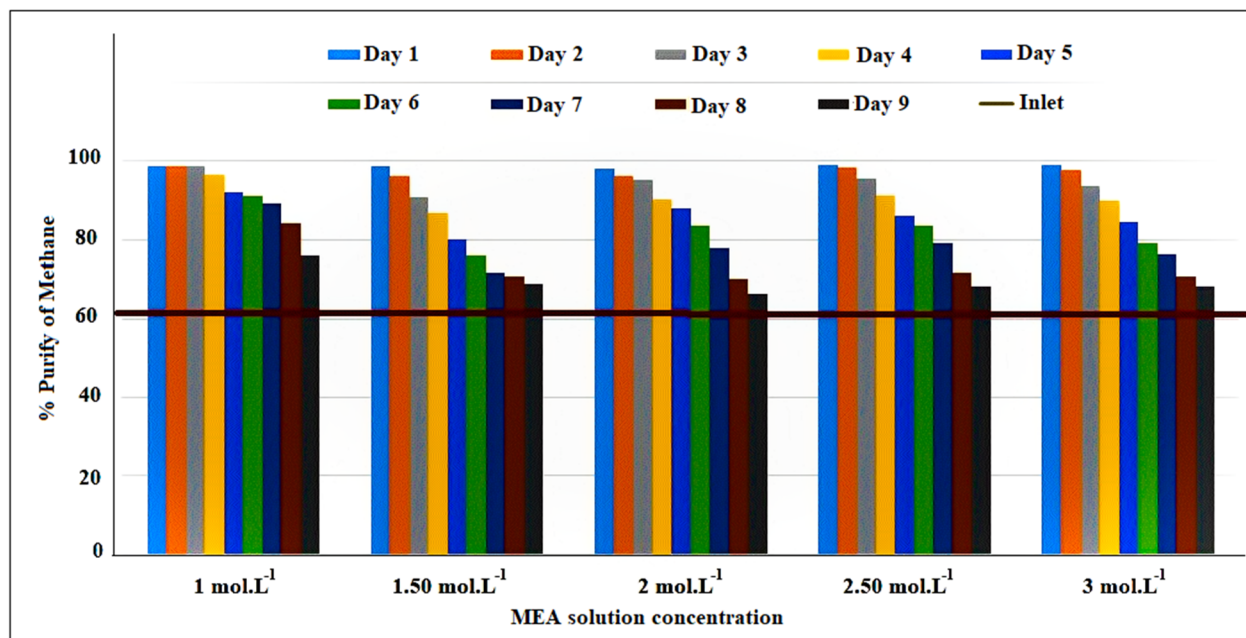
There are 4 columns of the small biogas purifier. The chemical absorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  were governed by iron rust and MEA solution respectively. Water scrubbing column was connected next to MEA column and finally physical adsorption by silica gel for decreasing moisture content. The saturated duration of biogas materials for  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and moisture eliminations was also determined from its output percentages of gases outlet were as same purify as the gases inlet with different MEA solution concentrations. The saturated duration represents the timing of purified materials utilization. It was predicted by linear regression analysis.

### 3. Results and Discussion

Components of biogas inlet consist by averaged of 61.10%  $\text{CH}_4$ , 37%  $\text{CO}_2$ , 0.90%  $\text{H}_2\text{S}$ , 0.30%  $\text{O}_2$ , and 0.70% others. Removal of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and moisture content in biogas using MEA solution, iron rust, and silica gel was performed under the real condition of biogas utilization for 2-strokes engine fuel. Inlet and outlet biogas from the packed columns using the biogas analyzer were measured including  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_2$ , and others comparing different concentrations of MEA solution. Table 1 shows the high concentration obtained the higher purity of  $\text{CH}_4$  according to higher  $\text{CO}_2$  removal same as by O. I. Maile et al. [3] that MEA concentration of 10%, 20% and 30% obtained  $\text{CH}_4$  purified of 76%, 78% and 85% respectively, corresponding to W. Kamopas et al. [9] and Ye et al, [10]. The concentration of MEA for 2 mol  $\text{L}^{-1}$  obtained the higher biogas purify than that of 1 mol  $\text{L}^{-1}$  [9]. It is not only the higher  $\text{CO}_2$  absorption but also the higher absorption rate [10]. The performance of purity for the concentration of 3 mol  $\text{L}^{-1}$  is higher than the concentration of 1 mol  $\text{L}^{-1}$ . The decreasing of % $\text{CH}_4$  content in Fig. 2 represented the performance of biogas improving for different MEA solution concentrations for 9 days of experiments. The  $\text{CH}_4$  purifying of the high concentration was a steeper decline than the low concentration. The saturated duration of each concentration of MEA solutions predicted by linear equations shows in Table 1 that the concentration of 1 mol  $\text{L}^{-1}$  has the longest. The outlet percentages of  $\text{CH}_4$  were above 90% due to the inlet percentage of about 61%. The saturated duration for the concentration of 1, 1.50, 2, 2.50, and 3 mol  $\text{L}^{-1}$  using linear regression analysis were 16.60, 10.20, 10.80, 11.10, and 10.60 days respectively. The  $\text{CO}_2$  removal performance for the concentration of 3 mol  $\text{L}^{-1}$  was 13.70% above the concentration of 1 mol  $\text{L}^{-1}$  comparing to using a concentration of 0.20 mol  $\text{L}^{-1}$  higher than 0.05 mol  $\text{L}^{-1}$  [9].

**Table 1** Biogas contents (%v/v) obtained with different concentrations of MEA solution volume of 2 L

MEA	Biogas Inlet (%VV <sup>-1</sup> )				Biogas Outlet (%VV <sup>-1</sup> )				Saturated duration equation
	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> S	O <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> S	O <sub>2</sub>	
1.0 mol L <sup>-1</sup>	61.50	36.40	0.90	0.30	91.30	7.30	0.04	0.40	$y = -2.62x + 104.86$ ( $r^2 = 0.88$ ) saturated 16.6 days
1.5 mol L <sup>-1</sup>	62.00	36.10	0.90	0.40	91.80	7.20	0.04	0.30	$y = -4.05x + 102.55$ ( $r^2 = 0.97$ ) saturated 10.2 days
2.0 mol L <sup>-1</sup>	61.80	37.10	0.90	0.30	92.10	6.90	0.05	0.30	$y = -4.10x + 105.63$ ( $r^2 = 0.96$ ) saturated 10.8 days
2.5 mol L <sup>-1</sup>	60.40	37.50	0.90	0.30	90.40	8.50	0.07	0.30	$y = -4.03x + 106.13$ ( $r^2 = 0.98$ ) saturated 11.1 days
3.0 mol L <sup>-1</sup>	59.90	37.90	0.80	0.30	92.50	6.30	0.07	0.30	$y = -4.14x + 105.09$ ( $r^2 = 0.99$ ) saturated 10.6 days

**Fig. 3** The capacity of CH<sub>4</sub> purity using different concentrations of MEA solution for 9 days

#### 4. Conclusion

Biogas utilization in engine and burner require the high purified methane due to its calorific value and non-corrosion. The improvement of biogas by removal CO<sub>2</sub> and H<sub>2</sub>S using MEA solution with different concentrations of 1 – 3 mol L<sup>-1</sup> obtaining the purified CH<sub>4</sub> maximum of 92.40%. The raw biogas contains by averaged of 61.10% CH<sub>4</sub>, 37% CO<sub>2</sub>, 0.90% H<sub>2</sub>S, 0.30% O<sub>2</sub> and 0.70% others. After passing through the biogas purifier with flowrate of 0.04 kg s<sup>-1</sup>, for MEA solution of 1 mol L<sup>-1</sup> obtained 91.70% CH<sub>4</sub>, 7.30% CO<sub>2</sub>, 0.04% H<sub>2</sub>S and 0.40% O<sub>2</sub>, and the saturated duration by 16.60 days. The

MEA solution concentration of  $1.50 \text{ mol L}^{-1}$  obtained 91.80%  $\text{CH}_4$ , 7.20%  $\text{CO}_2$ , 0.04%  $\text{H}_2\text{S}$  and 0.30%  $\text{O}_2$ , and the saturated duration by 10.20 days. The MEA solution concentration of  $2.0 \text{ mol L}^{-1}$  obtained 92.10%  $\text{CH}_4$ , 6.80%  $\text{CO}_2$ , 0.04%  $\text{H}_2\text{S}$  and 0.30%  $\text{O}_2$ , and the saturated duration by 10.80 days. The MEA solution concentration of  $2.50 \text{ mol L}^{-1}$  obtained 90.40%  $\text{CH}_4$ , 8.60%  $\text{CO}_2$ , 0.04%  $\text{H}_2\text{S}$  and 0.30%  $\text{O}_2$ , and the saturated duration by 11.10 days. The MEA solution concentration of  $1.50 \text{ mol L}^{-1}$  obtained 92%  $\text{CH}_4$ , 6.30%  $\text{CO}_2$ , 0.04%  $\text{H}_2\text{S}$  and 0.30%  $\text{O}_2$ , and the saturated duration by 10.60 days respectively. The  $\text{CO}_2$  removal performance for the concentration of  $3 \text{ mol L}^{-1}$  was higher than that of  $1 \text{ mol L}^{-1}$  by 13.70%. It was found that the higher concentration obtained the high purity performance for  $\text{CO}_2$  absorption but the  $\text{H}_2\text{S}$  purity performance was quite the same, while the saturated duration was small fluctuated. The saturated duration could be tested in condition of liquid/gas ratio.

## 5. Acknowledgement

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## 6. Reference

- [1] J. Cebula, Biogas purification by sorption techniques, *ACEE*. 2 (2009) 95 – 103.
- [2] O.I. Maile, H.E. Muzenda, H. Tesfagiorgis. Chemical absorption of carbon dioxide in biogas purification, *Procedia Manuf.* 7 (2017) 639 – 646.
- [3] O.I. Maile, H. Tesfagiorgis, E. Muzenda. The potency of monoethanolamine in biogas purification and upgrading, *SAJCE*. 24 (2017) 122 – 127.
- [4] A. Srichat, R. Suntivarakorn, K. Kamwilaosak. A development of biogas purification system using Calcium hydroxide and Amine solution, *Energy Procedia*. 38 (2017) 441 – 445.
- [5] F.R.H. Abdeen, M. Mel, M.S. Jami, S.I. Ihsan, A.F. Ismail. Improvement of biogas upgrading process using chemical absorption at ambient conditions, *J. Teknol.* 80 (1) (2018) 107 – 113.
- [6] O.W. Awe, Y. Zhao, A. Nzihou, D.P. Minh, N Lyezko. A review of biogas utilization, purification and upgrading technologies, *WASTE BIOMASS VALORI*. Springer. 8(2) (2017) 267 – 283.
- [7] B.F. Hulteburg, C. Persson, T. Tamm. Biogas upgrading-review of commercial technologies, *SGC Rapport*. 83 (2013) 270 – 277.
- [8] P. Kasikamphaiboon, J. Chungsiriporn, C. Bunyakan, W. Wiyaratn. Simultaneous removal of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  using MEA solution in a packed column absorber for biogas upgrading, *SJST*. 35 (6) (2013) 683 – 691.
- [9] W. Kamopas, A. Asanakham, T. Kiatsiriroat. Absorption of  $\text{CO}_2$  in biogas with amine solution for biomethane enrichment, *J. Eng. Technol.Sci.* 48(2) (2016) 231 – 241.
- [10] C. Ye, G. Chen, Q. Yuan. Process characteristics of  $\text{CO}_2$  absorption by aqueous monoethanolamine in a microchannel reactor, *Chin. J. Chem. Eng.* 20 (2012) 111 – 119.