

## AN OVERVIEW OF GAS-UPGRADING TECHNOLOGIES FOR BIOHYDROGEN PRODUCED FROM TREATMENT OF PALM OIL MILL EFFLUENT

IZZATI NADIA MOHAMAD<sup>1</sup>, ROSIAH ROHANI<sup>1\*</sup>,  
MOHD TUSIRIN MOHD NOR<sup>2</sup>, PIETERNEL CLAASSEN<sup>2</sup>,  
MUHAMMAD SYUKRI ABD. RAHAMAN<sup>1</sup>,  
MOHD. SHAHBUDIN MASTAR@MASDAR<sup>1</sup>, MASLI IRWAN ROSLI<sup>1</sup>

<sup>1</sup>Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

<sup>2</sup>UKM-YSD Chair for Sustainable Development, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

\*Corresponding Author: rosiah@ukm.edu.my

### Abstract

To date, a high energy demand has led to massive research efforts towards improved gas-separation techniques for more energy-efficient and environmentally friendly methods. One of the potential alternative energies is biogas produced from the fermentation of liquid waste generated from the oil-extraction process, which is known as palm oil mill effluent (POME). Basically, the gas produced from the POME fermentation process consists mainly of a CO<sub>2</sub> and H<sub>2</sub> gas mixture. CO<sub>2</sub> is known as an anthropogenic greenhouse gas, which contributes towards the climate change phenomenon. Hence, it is crucial to determine a suitable technique for H<sub>2</sub> separation and purification with good capability for CO<sub>2</sub> capture, as this will reduce CO<sub>2</sub> emission to the environment as well. This paper reviewed the current gas-separation techniques that consist of absorption, adsorption and a membrane in order to determine the advantages and disadvantages of these techniques towards the efficiency of the separation system. Crucial aspects for gas-separation techniques such as energy, economic, and environmental considerations are discussed, and a potential biohydrogen and biogas-upgrading technique for industrial POME application is presented and concluded in this paper. Based on the comparison on these aspects, water scrubbing is found to be the best technique to be used in the biogas-upgrading industry, followed by membrane and chemical scrubbing as well as PSA. Hence, these guidelines are justified for selecting the best gas-upgrading technique to be used in palm oil mill industry applications.

Keywords: Biogas, Biohydrogen, POME, Separation techniques.

**Nomenclatures**

A	Kinetic diameter
R	Radius
L	Thickness

**Abbreviations**

BOD	Biochemical Oxygen Demand
CMS	Carbon Molecular Sieve
CNTs	Carbon Nanotubes
COD	Chemical Oxygen Demand
DEA	Diethanolamine
EHC	Electrochemical Hydrogen Compression
FFB	Fresh Fruit Bunches
GPU	Gas Permeation Unit
HRT	Hydraulic Retention Time
GHG	Greenhouse Gases
HyET	Hydrogen Efficiency Technologies
ID	Internal Diameter
IGCC	Integrated Gasification Combined Cycle
MC	Membrane Contactor
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
NLPM	Normal Liter Per Minute
PEM	Polymer Electrolyte Membrane
POME	Palm Oil Mill Effluent
PSA	Pressure Swing Adsorption
SILMs	Supported Ionic Liquid Membranes
SLMs	Supported Liquid Membranes
SLPM	Standard Liter Per Minute
SMROG	Steam Methane Reforming Off-Gas
TEA	Triethanolamine
VSA	Vacuum Swing Adsorption

**1. Introduction**

Palm oil mill effluent (POME) is liquid waste generated from the oil-extraction process from fresh fruit bunches (FFBs) in palm oil mills [1], which originate from two main processes: (i) sterilization and (ii) clarification [2, 3]. POME consists of 95–96% water, 0.6–0.7% oil, and 4–5% total solids including 2–4% suspended solids [4]. This effluent is a thick brown liquid with a biochemical oxygen demand (BOD) and chemical oxygen demand (COD) 100 times higher than domestic sewage [2, 5-7], high solid concentrations, and high acidity [1, 8], which make the effluent highly polluting. The comparison of characteristics possess by domestic sewage and POME is listed in Table 1.

Thus, the treatment process of POME is crucial in order to minimize the large negative impact of POME on the environment. To date, POME treatment has evolved into a new dimension, enhancing simultaneous bioenergy recovery strategies such as energy recovery for electricity, heat, and transport which currently has been applied by other renewable energy sources such as from

biomass, biogases, and biofuels. Implementation of this approach could provide many benefits, as it will reduce the wastewater treatment cost by producing green energy sources as the by-products [9], including biohydrogen and biomethane. The common conventional approach for POME treatment, for example in the ponding system, has good potential for producing bioenergy. Further improvement of POME treatment includes aerobic and anaerobic digestion, physicochemical treatments, and membrane filtration [10].

**Table 1. Characteristics of domestic and sewage for raw and discharge standard.**

Parameter	Domestic Sewage		POME	
	Raw	Discharge standard	Raw	Discharge standard
	[11]	[12]	[13]	[13], [14]
COD (mg/l)	800	200	15000-100000	-
BOD (mg/l)	350	50	10250-43750	100
pH	4-5	5.5-9.0	3.4-5.2	5-9

POME treatment through the ponding system under aerobic conditions is simple and requires low-cost and low-energy input. However, this system has several drawbacks such as high area demand, low treatment efficiency, long hydraulic retention, high sludge production, and large emission of greenhouse gases (GHG), including methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) [15]. The optimization of the POME treatment system using a more efficient anaerobic digester could initiate POME to become one promising feed for producing renewable energy in Malaysia, as it can produce and capture valuable biogases such as biomethane and biohydrogen [1]. The treatment of wastewater is basically aimed at reducing the discharge in order to recycle the treated POME and capture the methane generated to reduce GHG emissions and, finally, to substitute the nonrenewable fuels currently consumed in the palm oil mill [15]. The common composition of biogas produced by several researchers is presented in Table 2.

Based on Table 2, the composition of biogas produced is dependent mostly on the Hydraulic Retention Time (HRT). At lower HRT, the biogas produced will consist of  $\text{H}_2$  and  $\text{CO}_2$  while for higher HRT the biogas produced will be  $\text{CH}_4$  and  $\text{CO}_2$ . This paper focuses on various technologies used for separation and purification (after this referred as upgrading) of biogas produced at lower Hydraulic Retention Time (HRT) which consists of  $\text{H}_2$  and  $\text{CO}_2$ . The focused biogas upgrading techniques are absorption, adsorption and membrane techniques. The advantages and disadvantages of these techniques are identified in this work from various literatures in order to find the most efficient separation system. Crucial aspects for gas separation technique such as energy, economic, and environmental considerations are discussed in details in order to determine the most potential biohydrogen and biogas upgrading technique from POME treatment in oil palm industry.

**Table 2. Composition of biogas produced by several researchers.**

POME fermentation condition	Composition of biogas produced (%)			Ref.
	$\text{CH}_4$	$\text{H}_2$	$\text{CO}_2$	
7 days HRT, 55 °C, mixed culture	70.1	-	20.9	[16]
2 days HRT, 55 °C, mixed culture	-	51.4	48.6	[17]
3 days HRT, 37 °C, mixed culture	-	50	50	[18]

## 2. Gas-Upgrading Techniques

The treatment process of POME used to reduce the COD before discharging into the environment releases mixed gases, comprising of CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub> [18]. The vastly increasing concentrations of CO<sub>2</sub> in the atmosphere has raised concerns with respect to the environment, which make mankind consider ways of controlling emissions of this GHG into the atmosphere. To date, CO<sub>2</sub> is considered the main anthropogenic contributor to the GHG effect, which is allegedly responsible for 60% of the increase in atmospheric temperature, commonly referred to as global warming [18, 19]. Among the various sources of CO<sub>2</sub>, fossil-fuel power plants are one of the major CO<sub>2</sub> contributors, which generate approximately 30% CO<sub>2</sub> from the production process [18]. Thus, critical development of effective methods for CO<sub>2</sub> capture and storage has become a major concern nowadays. The physical properties of CO<sub>2</sub> and H<sub>2</sub> (the major gases that will be discussed herein) are listed in Table 3 [20].

**Table 3. Physical properties of CO<sub>2</sub> and H<sub>2</sub> [20].**

Gas	Molecular weight (g mol <sup>-1</sup> )	Kinetic Diameter (Å)	Critical pressure (kPa)	Critical temperature (K)
CO <sub>2</sub>	44.0	3.30	7386	304.2
H <sub>2</sub>	2.0	2.89	1296	33.14

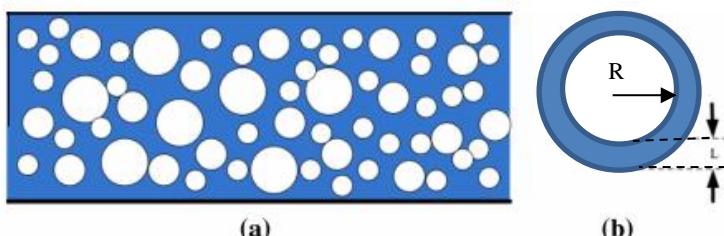
Recently, numerous methods of gas upgrading have been developed worldwide, including absorption, adsorption, and membrane technology [21]. Gas absorption using alkanolamine has been used for CO<sub>2</sub> scrubbing on an industrial scale for decades, but it brings several drawbacks as it is highly energy intensive and generates severe corrosion of the equipment involved [18]. Hence, better technology for gas separation is being developed for better separation performance. Currently, a novel technology for membrane separation has proven that it can be considered as one of the most potential technologies for biohydrogen separation and purification processes [22]. Membrane technology can play multiple roles in the development of biological systems as well as in fermentative biohydrogen technology. For example, membrane bioreactor employing a submerged or externally (loop) connected porous-water filtration (micro-, ultra-, nanofiltration and reverse osmosis) membranes are able to efficiently retain active biomass within the fermenter. Thus, it has been discovered that membrane technology could assist in overcoming the issue of low reaction yields by allowing *in situ* and continuous removal of biohydrogen using membranes from the membrane bioreactor [22].

Removal of accumulated biohydrogen at the top of the bioreactor is mostly required to be performed in a continuous system, mainly because of the high partial pressure of hydrogen formed during the fermentation process. It is believed that product inhibition may occur at certain biohydrogen concentrations and yields in the bioreactor [22, 23]. As the biohydrogen concentration increases in the bioreactor, the gas synthesis decreases and the metabolic pathways of the whole cell biocatalyst shifts towards the formation of other by-products, such as lactate, and other solvents, such as ethanol, acetone, butanol, and so on [22]. Therefore, purification and enrichment of biohydrogen is desirable in order to ensure optimal conditions for sustainable microbial biohydrogen production as well as an appropriate concentration of H<sub>2</sub> for its end use, for example, in fuel cells [23].

Thus, the following discussions will be focused on reviewing the techniques and the outcome from several gas-separation technologies conducted by different authors that have received great attention so far, which could each be used as a potential technology for biohydrogen and biogas upgrading in the treatment of POME. The main technologies included in this work are absorption, adsorption, and membrane technologies. Since the separation of gas mixture containing H<sub>2</sub> has been scarcely reported [24] (not many papers have reported on this so far), thus this paper will critically review on various gas mixture consist of at least H<sub>2</sub> or CO<sub>2</sub> such as CH<sub>4</sub>/CO<sub>2</sub> [25, 26], N<sub>2</sub>/CO<sub>2</sub> [27, 28] and other mixed gases [29] apart from the real mixture of H<sub>2</sub>/CO<sub>2</sub> which are targeted from POME treatment [17, 30]. Therefore the separation of CO<sub>2</sub> will be highlighted the most in this paper due to the said reason.

## 2.1. Absorption

Absorption refers to the separation process in which a gas is separated from a gas stream by using a liquid. Gases will come into contact with liquid and will be absorbed from the gas phase into the liquid phase in an absorption column [31]. Fig. 1 represents the schematic diagram of a gas–liquid dispersion system in a concurrent absorption process.



**Fig. 1. (a)** Schematic diagram of gas-liquid dispersion system in concurrent absorption and **(b)** Schematic diagram of mass transfer unit: bubble and liquid film around it [32].

During the gas–liquid micro-dispersion, Fig. 1(a), the gas/liquid flows along the channel and the relative velocity of the bubbles to the liquid phase is low [32]. Thus, multiphase dispersion flow could be considered as the accumulation of a large number of microdispersion units. Each mass-transfer unit consists of a bubble in the center with the radius designated as  $R$  and a liquid film around the bubble with the thickness designated as  $L$ , Fig. 1(b). During the separation of biohydrogen from a mixture of gases, CO<sub>2</sub> is usually absorbed into the stream, owing to the gas affinity and solubility towards the solvent used, rather than the hydrogen.

Absorption generally consists of two different processes, namely, physical and chemical process. For physical scrubbing, the process happens with no chemical reaction between CO<sub>2</sub> and the solvent in the gas mixture, but using an external energy, that is, pressure. Meanwhile, chemical scrubbing is based on dissolving CO<sub>2</sub> from biogas in solvent, and is further associated with a chemical reaction between the CO<sub>2</sub> and the solvent. In chemical scrubbing, the molecules of CO<sub>2</sub> are generally taken up by the volume of the solvent and not by the surface [33]. In chemical scrubbing, aqueous solutions, particularly alkanoamines, are commonly

used [34], which are known as the absorbent. In general, alkanolamines encompass the family of organic compounds of monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA) [35], which carry a hydroxy and amine functional group on an alkane backbone. Among these amines, the most commonly used is MEA, owing to its low cost [31]. The advantages associated with absorption by using alkanolamines include (i) the process can handle low CO<sub>2</sub> partial pressure gas streams and (ii) the technology is matured enough and reliable since there are already commercialized and available in the market [31].

On the other hand, the absorption process using alkaline solution as the absorbent has been extensively reported since the 1940s [36, 37]. This process has been used again recently as a way to reduce CO<sub>2</sub> emission in industry, through absorption of the CO<sub>2</sub> in the solution [38]. The most commonly used alkaline solution is hydroxide solution. The reaction that occurs at the initial CO<sub>2</sub> absorption time (first step) in an alkaline solution such as sodium hydroxide (NaOH) solution can be expressed using Eq. (1) [38]:



From Eq. (1), the CO<sub>2</sub> absorption reaction produces sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) as the main product and water as the by-product. Subsequently, as CO<sub>2</sub> is continuously fed into the NaOH solution, the Na<sub>2</sub>CO<sub>3</sub> will also react with the CO<sub>2</sub>. At this second step, the overall absorption reaction can be expressed as Eq. (2):

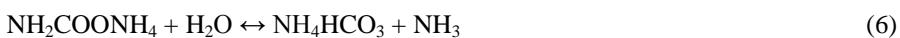


After reaction (2) reaches equilibrium, a slight amount of CO<sub>2</sub> may be absorbed, additionally, to physically cover up the shortage of unabsorbed CO<sub>2</sub> in water during this reaction. Finally, as NaOH becomes the limiting reactant, the total reactions of Eqs. (1) and (2) can be summarized by Eq. (3):



Hence, based on Eq. (3), the final product obtained from the absorption process between CO<sub>2</sub> and NaOH solution is sodium bicarbonate (NaHCO<sub>3</sub>), which has various applications, such as it can be used as a food additive.

Another solution commonly used as the absorbent in the absorption process is ammonia (NH<sub>3</sub>). The process starts when the CO<sub>2</sub> gas is transferred into the ammonia solution by physical absorption before reacting with NH<sub>3</sub>. The first product formed from this reaction is ammonium carbamate, which is easily hydrolyzed, whereby the main products are ammonium carbonate and ammonium bicarbonate [39]. The reaction sequences involved in the process are presented in Eqs. (4) to (8):



and the overall reaction can be described as Eq. (9):



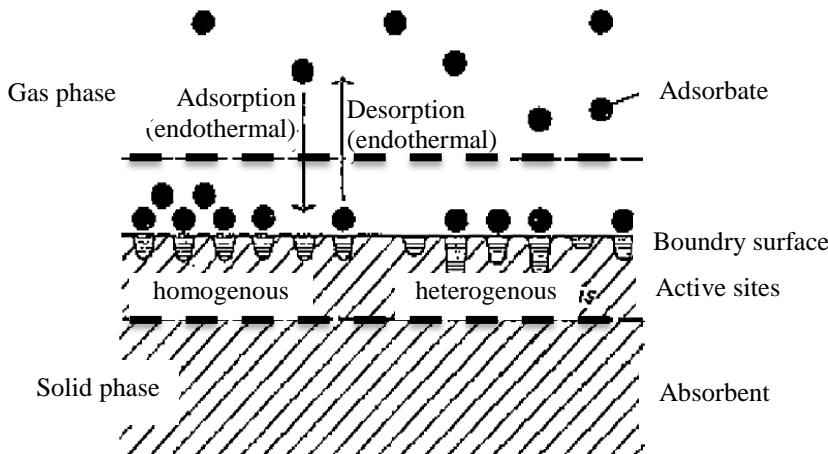
Using ammonia solution as the absorption solvent has many advantages such as there is less degradation to the environment, a higher absorption efficiency in terms of removal of one gas from the gas mixture, and there are no issues in terms of equipment corrosion [31].

Based on this finding, though various absorbents have been reportedly used for absorbing the CO<sub>2</sub> in an open literature, the best absorbent is still depending on ones' need whether efficiency, simplicity, economic, environment, safety and others are of main concern.

Furthermore, though the absorption technique has widely been used in industrial process for CO<sub>2</sub> absorption in various commercial applications, there is still limited application in terms of separation and purification of H<sub>2</sub> from gas mixtures containing CO<sub>2</sub>. Hence, more research on the separation of H<sub>2</sub> from CO<sub>2</sub> must be conducted in order to determine the suitability of this technique and its absorbent to be used in real industrial applications.

## 2.2. Adsorption

The next process that is well reported and used in industry for gas/liquid removal is adsorption. It is a process in which molecules of gas or liquid will contact and adhere to a solid surface in order to be adsorbed from the stream. Basically, it is the enrichment process of gaseous or dissolved substances (the adsorbate) on the boundary surface of a solid (the adsorbent). The active centers on surface adsorbents are where the binding forces between the individual atoms of the solid structure are not completely saturated. At these centers, the adsorption of foreign molecules takes place. In order to understand the adsorptive solvent recovery, some fundamentals of adsorption and desorption must be considered, as shown in Fig. 2 [40].



**Fig. 2. Schematic of adsorption and desorption process [40].**

Based on this figure, the adsorption of a gas or adsorbate on a solid surface follows three steps. Firstly, the adsorbate (ions in the case of a solution) is transported from the bulk to the external surface of the adsorbent. Secondly, the

adsorbate is passed through the solid surface, and lastly, it interacts with the surface atoms of the solid leading to (i) chemisorption (strong adsorbate–adsorbent interactions equivalent to covalent bond formation) or (ii) weak adsorption (weak adsorbate–adsorbent interactions, very similar to van der Waals forces) [40]. In the case of porous solids, after passing the adsorbate through to the external surface, the adsorbate will slowly diffuse into the pores and be adsorbed [41]. This will allow the gases to be collected from the product stream.

Generally, cyclic processes involve continuous CO<sub>2</sub> capturing processes and are often studied and applied to gas separation especially for adsorption techniques [33]. Cyclic processes involve the exchange of an adsorbent in the absorption and desorption steps. This switching is done by manipulating the pressure and temperature. Pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) are two types of adsorption processes available in the market [33]. PSA is a process in which the feed gas is compressed substantially above atmospheric pressure to allow CO<sub>2</sub> to be recovered at atmospheric pressure later on. This adsorption process is basically performed at pressures higher than atmospheric, whereas the desorption process occurs at atmospheric pressure. On the other hand, VSA is a process where the feed is slightly compressed up to a maximum of 1.5 atm and the CO<sub>2</sub> is recovered under vacuum conditions. This means that the adsorption takes place at near ambient temperature and desorption happens at lower pressure [29, 33, 42].

The PSA modelling framework was reported by Nikolic et al. [43] to design and model several PSA configurations for the production of H<sub>2</sub> and CO<sub>2</sub> from steam methane reforming off-gas (SMROG). Based on their study, new and modified PSA cycle configurations consisting of two groups of adsorption columns undergoing three cycle configuration steps have been designed and simulated, with the difference being in the number of beds and the type of the pressure equalization steps used compared to the existing process [43]. These new configurations offer high H<sub>2</sub> and CO<sub>2</sub> purity and recovery (H<sub>2</sub> of 99.99% purity and 86.04% recovery, and CO<sub>2</sub> of 99.94% purity and 86.21% recovery). These data showed that the new design configurations could give a comparable separation quality to the existing industrial systems and provide great alternatives for the adsorption technology. Hence, the application of these configurations to the POME treatment in the palm oil industry could represent huge potential for use in the future.

A summary of the gas-upgrading techniques using PVA and PSA, in terms of their gas compositions, absorbents, operating conditions, and recovery obtained from different reports, is presented in Table 4. Many authors such as You et al. [44], Lopes et al. [48], Ahn et al. [49], Casas et al. [52], Garcia et al. [54], and Casas et al. [56] have conducted a study on separation and purification for mixture gas of H<sub>2</sub> and CO<sub>2</sub>. It was found that You et al. [44] achieved the highest recovery among other studies (presented in Table 4) with 99.99% H<sub>2</sub> purity and 80% recovery. Their work was conducted using the cyclic sequences for the two-bed PSA and pressure VSA (PVSA) processes, with activated carbon as the absorbent. The PVSA process, which combined vacuum and purge/swing steps, could improve the recovery by about 10% compared to the PSA process, which is believed to be the factor responsible for achieving the good recovery in this study. At present, activated carbon is used a lot in commercial applications and is the most investigated material for absorbents [18].

**Table 4. Summary of gas upgrading via PSA and VSA techniques.**

<b>Feed Compositions</b>	<b>Number of bed; material; dimension</b>	<b>Absorbent</b>	<b>Operating conditions</b>	<b>Recovery</b>	<b>Ref.</b>
CO <sub>2</sub> :CH <sub>4</sub>	1bed 18cm length 4cm diameter Glass column	Activated Carbon Fibers (ACF)	Atm. pressure 77K 0.6-1.0 SLPM	CO <sub>2</sub> selectivity (CO <sub>2</sub> /CH <sub>4</sub> ) of 2.2 with total CO <sub>2</sub> absorbed 0.7 mmol	[25]
34% CO <sub>2</sub> 66% CH <sub>4</sub>	1bed 0.19m length 0.016m ID 2 mm column wall thickness	Sepiolite clay mineral	1.2x10 <sup>5</sup> Pa	>97% CH <sub>4</sub> purity	[26]
13-16% CO <sub>2</sub> 84-87% N <sub>2</sub> (Purity 99.95%)	1bed 105 mm length 10 mm ID	Zeolite and CuBTC	35°C 0.26 NLPM 600 s breakthrough time	For 40% breakthrough time: 68% CO <sub>2</sub> Purity (Zeolite) 63% CO <sub>2</sub> Recovery (CuBTC)	[27]
44.9% v/v CO <sub>2</sub> 55.1% v/v CH <sub>4</sub>	tubular quartz reactor, filled with 1.35 g of adsorbent material in pellets	Na-LTA (4A) and Na-FAU (13X) zeolite	Room temperature	>80% CO <sub>2</sub> recovery	[45]
88% Dry air 12% CO <sub>2</sub>	3 beds Stainless steel 1m Length 7.7 cm ID 5 mm wall thickness	13X zeolite	Between 40°C and 50°C	>90% CO <sub>2</sub> purity >60% CO <sub>2</sub> recovery	[29]
96.5% He 3.5% CO <sub>2</sub>	11.62 m length 7.38 m diameter	Activated carbon honeycomb monolith	310 K	89.7% CO <sub>2</sub> purity 70% CO <sub>2</sub> recovery 1.9GJ/ton	[46]
17% v CO <sub>2</sub> 83% v N <sub>2</sub>	Stainless steel reactor 203mm height 9mm diameter	Olive stones and almond shells	303 K 130kPa	97% CO <sub>2</sub> recovery	[28]
15% CO <sub>2</sub> 85% N <sub>2</sub>	0.202 m length	Zeolite 5A	298 K	96% CO <sub>2</sub> purity	[47]
99% H <sub>2</sub> mixture and 95% H <sub>2</sub>	2 beds Stainless steel	Activated carbon	3 SLPM 6.5 – 9.5 bar	99.99% H <sub>2</sub> purity; 80% recovery 99.96% H <sub>2</sub>	[44]

mixture	100 cm long and 2.15 cm ID		0.1 – 0.2 P/F	purity; 78.4 recovery	
0.7 H <sub>2</sub> molar fraction and 0.73 H <sub>2</sub> molar fraction	1 bed 0.267 m height	Activated carbon	0.1 SLPMP and 5 SLPMP 0.1 – 5 bar 25 – 150 °C	99.981% H <sub>2</sub> purity 81.6% recovery	[48]
H <sub>2</sub> :CO <sub>2</sub> : CH <sub>4</sub> :CO: N <sub>2</sub> (0.38:0.5: 0.01:0.01: 0.1 vol.%)	2 and 4 beds Stainless steel 100 cm long and 3.5 cm ID	Zeolite and activated carbon	0.1 – 0.3 P/F 20 – 25 °C 5 – 10 bar 3 – 7 SLPMP	96 – 99.5% H <sub>2</sub> purity 71-85% recovery	[49]
80% CO <sub>2</sub> 20% N <sub>2</sub>	1 bed Stainless steel 0.3m length 0.027m ID	Activated Carbon, Carbon Molecular Sieve (CMS), Zeolite 13X	298 K 211 kPa 220s Cycle time	Zeolite 13X: >99% Purity >85% Recovery CMS: >95% Purity >40% Recovery	[50]
12% CO <sub>2</sub> 88% N <sub>2</sub>	1 bed	Zeolite 13X	1 atm 30 °C	91% purity	[51]
60% H <sub>2</sub> 40% CO <sub>2</sub>	120 cm length 5 cm ID	Activated Carbon	34 bar 35 °C	88% purity	[52]
15% CO <sub>2</sub> 85% N <sub>2</sub>	30 cm height 2.2 cm diameter	Carbon Nanotubes (CNTs)	25 °C-100 °C	97% purity	[53]
CO <sub>2</sub> :H <sub>2</sub> : N <sub>2</sub> (40:50:10 vol.%)	1 Bed 9×10 <sup>-3</sup> m diameter	Activated Carbon	15 bar 45 °C 100 mL min <sup>-1</sup> (STP)	91.5% purity	[54]
CO <sub>2</sub> :N <sub>2</sub> : O <sub>2</sub> :Ar: SO <sub>2</sub> :H <sub>2</sub> O (14.27:77. 84.461:0. 94:0.004: 2.33 vol %)	10 m height 8 m diameter	Zeolite	1 bar 20 °C	93% purity 90.9% recovery	[55]
50% CO <sub>2</sub> 50% H <sub>2</sub>	1.2 m length 0.025 m diameter	USO-2-Ni MOF and UiO- 67/MCM- 41 hybrid	34 bar 35 °C	USO-2-Ni MOF: 89.5% purity 67/MCM-41 hybrid: 87.5% purity	[56]

### 2.3. Membrane technology

Membrane-based technology has great advantages over other gas-upgrading systems and in terms of overcoming the difficulties for capturing CO<sub>2</sub> and for enhancing the H<sub>2</sub>

purity in various gas mixture such as biogas mixture [21]. Membrane technology also has the ability to separate chemical species without a phase change, with low thermal-energy requirements, and with a convenient startup and shutdown procedure [21]. Currently, there are wide ranges of membranes available for hydrogen-separation applications, which can be classified into organic (polymer) membranes and inorganic (ceramic, metal, glass, clay and carbon molecular sieve) membranes [57]. These groups can then be subdivided into porous and nonporous membranes. Basically, the performance of a membrane system is largely determined by the characteristics of permeability and selectivity [21, 58, 59]. Permeability is the flux of a specific gas through a membrane, whereas selectivity is the preference of the membrane to pass one gas species over another [58].

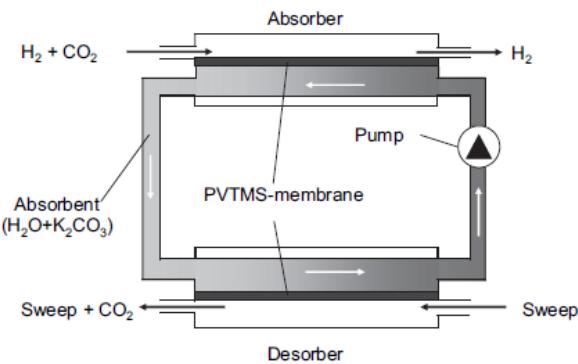
### 2.3.1. Membrane contactor

Nondispersive absorption using a gas–liquid contactor is a traditional absorption method performed in scrubbers. This system is currently being used in a Membrane Contactor (MC), which consists of a porous, organic (polymeric) membrane that stands as a physical barrier between the gases to be separated and the absorption liquid such as an aqueous solution of potassium carbonate ( $K_2CO_3$ ). The separation is dependent on the attraction of gases to the absorbent employed and, therefore, MCs can be described as devices combining membrane and absorption technology, benefiting from the advantages of both technologies [22, 60]. A MC is a novel type of gas–liquid contactor, which gives the possibility to provide a defined mass-transfer area, larger interfacial area per volume, and independent control of the gas and liquid flow rates without flooding and foaming [61]. The flow of the gas and liquid phase is well separated by the membrane. The area of the membrane corresponds to the mass-transfer area. By choosing proper geometries of the membranes, a high volume-related area and low pressure drops can be achieved in both phases [61].

A MC module for  $CO_2/H_2$  consists of an absorber and a desorber with a continuous absorbent flow, as adapted from Beggel et al. [61] and presented in Fig. 3. The membrane used by Beggel et al. for the unit is a polyvinyl trimethylsilane (PVTMS) membrane, which was synthesized in-house. PVTMS polymer has been known for more than 40 years as a polymer with a reasonable  $CO_2$  permeability at pressures of 40 to 44 bar [62]. In the MC system, external energy is necessary in the desorption unit in order to increase the temperature of the absorbent and to circulate the liquid using a pump. The  $CO_2$  in the  $H_2/CO_2$  gas mixture entering the absorber permeates through the membrane and is absorbed by the liquid absorbent. The other gas component remains in the gas phase (unabsorbed) and leaves the absorber as a clean gas. The loaded absorbent is pumped to the desorber where the sweep gas ( $N_2$ ) is introduced to transport  $CO_2$  out from the membrane contactor whereby the absorbent will proceed for regeneration and will be transported back to the absorber to allow continuous MC operation [60, 61].

On the other hand, Modigell et al. [60] reported on the separation of  $H_2$  from  $CO_2$  using a membrane contactor in biohydrogen production. In this work, a PVTMS membrane with a dense layer of 0.2  $\mu m$  in thickness and PTMSP membrane of 10  $\mu m$  were used. Both PVTMS and PTMSP are amorphous glassy polymers with glass transition temperatures of  $T_g = 155^\circ C$  and  $T_g = 230^\circ C$ , respectively. From the experiments it was pointed out that the developed

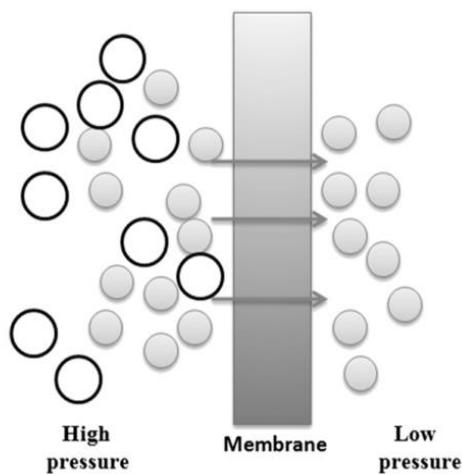
membranes possessed high gas permeabilities and hence, they can be used for membrane contactors in the field of biohydrogen purification as intended. However, among these two membranes it was found that the synthesized PVTMS membranes are the most suitable materials for effectively separating biohydrogen from the H<sub>2</sub>/CO<sub>2</sub> mixture. The membranes used in this work possessed high CO<sub>2</sub> permeability using 1 M K<sub>2</sub>CO<sub>3</sub> aqueous solution as the absorbent [63]. Hence, it is believed that this technique has high potential to be used for the upgrading of biohydrogen from H<sub>2</sub>/CO<sub>2</sub> mixtures produced from POME fermentation.



**Fig. 3. Schematic diagram of the CO<sub>2</sub>/H<sub>2</sub> separation using a membrane contactor [61].**

### 2.3.2. Membrane gas permeation

The membrane used in a gas-permeation unit is responsible for gas separation, as it determines the permeability and selectivity of the process. The permeation process will occur by contacting the gas and the solid (membrane). Hence, no liquid is required as the solvent during the permeation process, unlike the one used in MC. According to Luis et al. [64] the important components for gas permeation include the permeability of the gas mixture, the separation factors, the structure and thickness (permeance), the membrane configuration (i.e., flat, hollow fibers), as well as the module and system design, which include many variables to be studied. Organic polymers, as asymmetric nonporous membranes, are typically used for gas separation. The driving force of CO<sub>2</sub> permeation through a gas membrane is the partial pressure difference between the feed and the permeate side (Fig. 4) [65]. The major challenge to be overcome for their implementation in industry is the large scale of the process with large membrane areas, owing to the high volume of the gas stream to be treated, and the low concentration of CO<sub>2</sub> in the gas stream that leads to a low CO<sub>2</sub> driving force [65]. There are ways to increase the driving force: (i) increase the feed pressure using a compressor, (ii) increase the CO<sub>2</sub> concentration in the feed by recirculating an enriched CO<sub>2</sub> stream, (iii) decrease the permeate pressure using a vacuum pump, and (iv) decrease the CO<sub>2</sub> concentration in the permeate using a sweeping gas [65]. However, these involve high energy-consumption costs. Therefore, an economic evaluation is essential for the overall process under specific operating conditions in order to find the best alternative processes or techniques.



**Fig. 4. Principle of gas separation membrane via pressure driving force [65].**

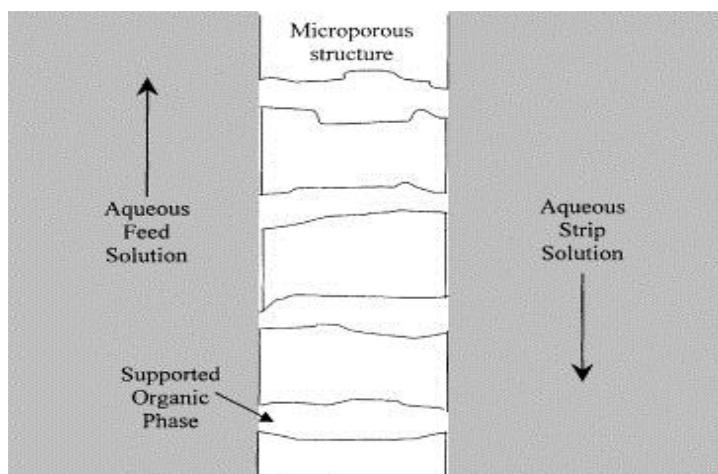
Kumbharkar et al. [66] demonstrated H<sub>2</sub> and CO<sub>2</sub> separation at high temperatures (up to 400°C) using a developed polybenzimidazole (PBI)-based asymmetric hollow-fiber membrane. With an increase in temperature, these membranes showed a relatively large increase in H<sub>2</sub> permeance compared to CO<sub>2</sub> permeance, thereby enhancing the H<sub>2</sub>/CO<sub>2</sub> selectivity at higher temperatures. This effect was attributed to the rigid structure of the PBI polymer and the smaller kinetic diameter of H<sub>2</sub> compared to CO<sub>2</sub>, which led to increase diffusion as the temperature increased. The highest H<sub>2</sub> permeability was recorded at 400°C with 2.6 GPU and a H<sub>2</sub>/CO<sub>2</sub> selectivity of 27.3. These results depicted that PBI, in combination with its excellent inherent properties (high thermal stability and rigid structure) and ability to show good separation characteristics, is an attractive and potential candidate for high-temperature H<sub>2</sub>/CO<sub>2</sub> separation. Thus, these developed membranes could have potential in the future for the purification of biohydrogen produced from POME fermentation.

### 2.3.3. Supported liquid membranes (SLMs)

SLM systems represent another type of membrane in which a defined solvent or carrier solution immobilizes and embeds inside the porous structure of a polymeric or ceramic membrane [67-69]. This solution stays in the porous structure by capillary forces, which separate the feed phase from the receiving phase, as illustrated in Fig. 5 [67-69]. The transport of the permeating species occurs through a solution diffusion/mass-transfer mechanism [69]. This configuration has received great attraction, because it combines the processes of extraction and stripping into one single stage, and the amount of solvent used is much less than in conventional solvent-extraction process [67, 70].

However, SLM is rarely and scarcely applied in industry, mainly owing to concerns about SLM stability and long-term performance, leading to a reduction in gas permeance, solute flux, and membrane selectivity [67, 69-71]. These events happen because of the loss of solvent (organic phase) from the supporting

membrane, either by evaporation or dissolution/dispersion into the adjacent phases, pressure differences, emulsion formation, or attrition of the organic film through lateral shear force [68, 70-72]. Recent studies have suggested the use of ionic liquids (ILs) to overcome these drawbacks [72]. ILs are thermally stable liquid salts at room temperature, which constitute an organic cation and either an organic or an inorganic anion. The use of ILs as immobilized phases in porous supports produces supported ionic liquid membranes (SILMs), which are particularly interesting, owing to their nonvolatile properties under most conditions and because ILs are insoluble, which lead to stable SLMs without any observable loss of the ILs to the atmosphere or the contacting gas phases [67, 72]. SILMs possess a higher stability than conventional SLMs, because of the greater capillary forces associated with the high viscosity of ILs, which could reduce the displacement of the liquids from the micropores under pressure. In addition, the utilization of ILs as membrane-supported materials could make the permeance of the gas components different in terms of the receiving phase [67].



**Fig. 5. Schematic diagram of a general supported liquid membrane process [67].**

Separation of CO<sub>2</sub> and H<sub>2</sub> mixtures using facilitated SILMs at high temperatures was presented by Myers et al. [73]. An amine-functionalized IL encapsulated in a SILM was reported used to separate CO<sub>2</sub> from H<sub>2</sub> with a higher permeability and selectivity was recorded than any common membrane system [73]. This separation was accomplished at elevated temperatures using facilitated transport SILMs. The selectivity was found to increase with increasing temperature. At separation temperatures of 85°C and above, initially, complex dissociation (CO<sub>2</sub> molecular network breakup with ILs) overshadowed the CO<sub>2</sub> separation, but after some time, it was eclipsed by CO<sub>2</sub> diffusion as the rate-limiting step in the separation. The effect is enhanced by a simultaneous breakup of the molecular CO<sub>2</sub> network formerly present in the IL, which leads to an increase in H<sub>2</sub> permeability. The maximum selectivity corresponds to the lowest temperature at which the complex readily dissociates. At temperatures above 85°C, the selectivity shows the expected decrease with temperature, which is associated with the domination of diffusive selectivity over solubility selectivity at high temperatures,

normally observed in solution diffusion membranes. This finding has shown the potential of the SLM technique to be used in the purification and separation of biohydrogen produced from POME fermentation in near future. Reasonable temperatures and operating conditions of the SLM system are expected to give a desirable CO<sub>2</sub>/H<sub>2</sub> separation.

#### **2.3.4. Electrochemical hydrogen compression (EHC) using catalyzed membrane**

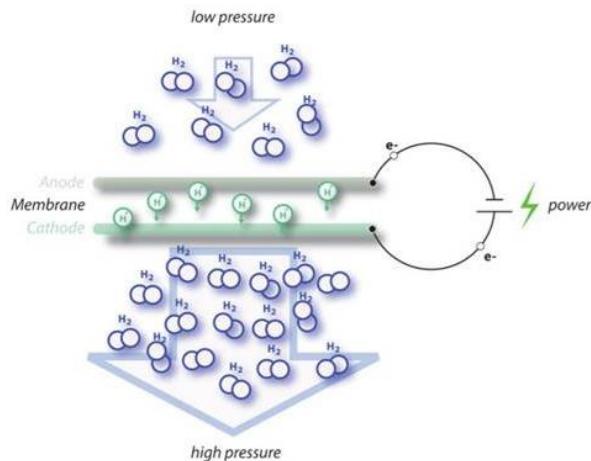
Membrane technology using membrane gas permeation and a MC is commonly reported to separate biohydrogen from CO<sub>2</sub> [65]. However, a catalyzed membrane separation technique with EHC is new and currently receiving great attention for the separation and purification of H<sub>2</sub> from mixed gases [74]. This EHC technology is registered under the name of HyET (Hydrogen Efficiency Technologies), which was founded in 2008 by the late inventor, Sir Erik Middelman in Arnhem, The Netherlands. HyET has made significant progress, making proprietary membranes and membrane cell systems specifically for EHC. HyET obtained the first compression breakthrough at a pressure 400 bar in early 2010, selectively extracting and purifying any H<sub>2</sub> content. Later on, it was superseded by a pressure of 800 bar in 2011, and then the pressure even reached 1000 bar in 2013. EHC is particularly suitable for purifying H<sub>2</sub> from mixtures, as it enables operation across a wide range of operating pressures [74].

EHC compressors use a direct current (DC) to pull the H<sub>2</sub> through an impermeable membrane. This technology is very efficient and highly selective for hydrogen. Only H<sub>2</sub> molecules that come into contact with the catalyzed membrane surface are freely dissociated into two protons (H<sup>+</sup>) and two electrons (e<sup>-</sup>). Protons diffuse through the acid membrane, whereas the electrons travel through an external circuit when a current is applied. At the opposite catalyzed membrane surface, the protons and electrons recombine to form hydrogen molecules again. This process continues as long as the driving force behind the current exceeds the internal energy. This mechanism allows only H<sub>2</sub> transport across the membrane, which means that other gaseous species are effectively filtered out. Therefore, the hydrogen is purified. Further details on the type of membrane and catalyst used in their system are not disclosed. Fig. 6 shows the illustration of the overall EHC process.

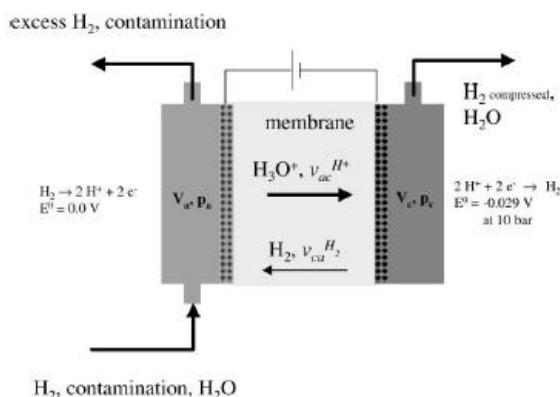
EHC developed by HyET has a superior advantage, as it can transport H<sub>2</sub> against its concentration gradient at pressure ranges from 1 – 700 bar. By having this advantage, it can transport from low to high concentrations of H<sub>2</sub> by using an electrical current as the driving force. In addition, the electrochemical removal of H<sub>2</sub> directly from the reactor greatly improves the productivity of hydrogen-producing bacteria [74]. By doing so, other gases, such as CO<sub>2</sub> from the gas stream in the fermentation process, could be purified in the retentate stream and further utilized.

Similar technologies were also reported by Ströbel et al. [75]. They described a system that uses an electrochemical cell for the compression of hydrogen. This electrochemical hydrogen compressor operates at a lower hydrogen flux than mechanical hydrogen compressors. Further development of the polymer electrolyte membrane (PEM) fuel cell could afford good prospects for realizing electrochemical compression on a competitive basis. A specialized gas-diffusion layer established the possibility to pressurize the cathode volume up to 54 bar [75].

The working principle of EHC is shown in Fig. 7. Owing to the applied potential difference, hydrogen at pressure  $P_a$  (from the left cell) is oxidized at the anode to  $H^+$ , transported through the PEM, and reduced at the cathode to hydrogen at pressure  $P_c$  (refer to Fig. 7). If the cathode compartment ( $V_c$ ) is tightly sealed, the formation of hydrogen at the cathode results in an increase of the pressure  $P_c$ . The advantages of the electrochemical system, apart from the efficiency, include the noiseless operation, purified hydrogen produced, and simplicity of the cooling system.



**Fig. 6. EHC process using an electrolyte catalysed membrane in presence of voltage [74].**



**Fig. 7. Principle of the electrochemical hydrogen compressor [75].**

Other research performed by Grigoriev et al. [76] concerned the development and characterization of an EHC based on PEM technology. In their compression system, pure  $H_2$  was supplied to the anode, and then pure pressurized (potentially several hundred bars)  $H_2$  was collected at the cathode. Based on this study, EHC has been targeted for extracting hydrogen from different gas mixtures and waste gases such as from outlet gases of fuel cells and products of organic fuel conversion. Various operating parameters such as water vapor partial pressure, current density, and

operating temperature on the maximum output pressure are of concern and should be addressed for such EHC [76]. The maximum output pressure of PEM hydrogen EHC was calculated as a function of membrane thickness, current density, and operating temperature. It was found that the most significant parameters to be considered for designing and operating a hydrogen compressor are current density, operating temperature, and membrane thickness [76].

The gas upgrading using membrane techniques are summarized and presented in Table 5. Different gas combinations and membrane materials were used in the studies. Many authors such as Modigell et al. [60], Kumbharkar et al. [66], Smart et al. [79], Sandström et al. [80], Ramírez-Morales et al. [81], Qi et al. [83], Franz and Scherer [86], Wang et al. [91], and Xing and Ho [92] have conducted a study on separation and purification for mixture gas of H<sub>2</sub> and CO<sub>2</sub>. The highest selectivity for H<sub>2</sub> over CO<sub>2</sub> was obtained by Wang et al. [91] with selectivity of 28 at 25 oC (1 bar) using aminated titania nanotubes into sulfonated poly(ether ether ketone) membrane. The permeability of H<sub>2</sub> recorded was  $2.5 \times 10^3$  barrer. The finding is followed by Kumbharkar et al. [66] with a selectivity of 27.28 at a temperature of 400°C using PBI hollow fiber membranes. Under these conditions, the best permeance for CO<sub>2</sub> and H<sub>2</sub> were 0.096 and 2.6 GPU, respectively. On the other hand, Teramoto et al. [77] reported CO<sub>2</sub> separation and concentration by using a capillary-type facilitated membrane for a mixture of CO<sub>2</sub> and N<sub>2</sub>. The recovery and purity of CO<sub>2</sub> were 76% and 99.8%, respectively. The selectivity of CO<sub>2</sub> over N<sub>2</sub> was up to 8000. For separation between CO<sub>2</sub> and CH<sub>4</sub>, Blinova and Svec [78] found that CO<sub>2</sub> permeability over CH<sub>4</sub> is 3460 higher with a selectivity of 540 for a feed gas of 90% CH<sub>4</sub>/10% CO<sub>2</sub> at 128 kPa.

**Table 5. Summary of gas upgrading via membrane separation techniques.**

Technology	Condition	Recovery	Ref.
MC for efficient CO <sub>2</sub> removal, MEA as liquid carriers	79% CO <sub>2</sub> , 21% H <sub>2</sub>	92% H <sub>2</sub> purity CO <sub>2</sub> 35700 barrer H <sub>2</sub> 7100 barrer	[60]
Cobalt oxide silica membrane	Feed binary mixture of H <sub>2</sub> /CO <sub>2</sub> for 90/10 and 80/20 at 600°C	Permeate gas concentration $\geq$ 98 vol%	[79]
Poly benzimidazole based asymmetric hollow fiber membrane	Pure gases of H <sub>2</sub> and O <sub>2</sub> were tested in sequence at 400 °C	H <sub>2</sub> permeance 2.6 GPU CO <sub>2</sub> permeance 0.096 GPU Selectivity (H <sub>2</sub> /CO <sub>2</sub> ) 27.28	[66]
MFI membrane for CO <sub>2</sub> separation	Equimolar CO <sub>2</sub> /H <sub>2</sub> mixtures, total pressure of 600-3000 kPa with ratio of 5 at room temperature (295 K). The pore size of MFI:0.55 nm, thickness: 0.7 um.	The highest CO <sub>2</sub> flux was $657 \text{ kgm}^{-2}\text{h}^{-1}$ at total feed pressure 3000 kPa, highest CO <sub>2</sub> permeance is $93 \times 10^{-7} \text{ mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ at total feed pressure 1000 kPa.	[80]

Two gas membrane modules for fermentative H <sub>2</sub> separation: PDMS and SAPO-34	Feed gas: 10% H <sub>2</sub> , 90%CO <sub>2</sub> . Pressures ranging from 10 to 80 kPa, Different feed pressures of 110 to 180 kPa, permeate pressure at 101.3 kPa, 296K.	H <sub>2</sub> concentration in retentate 14.68% (feed pressure 180 kPa), mean values of permeability coefficients CO <sub>2</sub> 3285 ± 160 and H <sub>2</sub> 569 ± 65 barrer	[81]
Multi tube membranes at high temperature for H <sub>2</sub> and Ar separation	Operate at 400°C for binary gas mixture separation. The feed and permeate pressure: 6 atm and 1 atm respectively.	For feed of 0.8H <sub>2</sub> and 0.2Ar: 97.07 H <sub>2</sub> yield 0.96 H <sub>2</sub> purity 0.61 H <sub>2</sub> recovery	[82]
PANI composite membranes for CO <sub>2</sub> and CH <sub>4</sub> separation	Feed gas: 90% CH <sub>4</sub> , 10% CO <sub>2</sub> . Operating gas pressure 128 kPa for the (feed) less than 100 kPa (permeate). He as sweep gas.	CO <sub>2</sub> permeability 3460 Barrer Selectivity 540	[78]
MC with dense membranes for CO <sub>2</sub> separation using K <sub>2</sub> CO <sub>3</sub> , piperazine (PZ) as absorption medium.	15 vol% CO <sub>2</sub> and 85 vol% N <sub>2</sub> , liquid flow rates of 1-20 ml min <sup>-1</sup> and a constant feed gas flow of 200 ml min <sup>-1</sup> . Absorption temperature is 25°C.	0.5M K <sub>2</sub> CO <sub>3</sub> /0.5 M PZ removes CO <sub>2</sub> almost completely. End concentration in the retentate is 0.01 at 5 ml min <sup>-1</sup> .	[61]
Microporous Niobium-BTESE hybrid silica membrane	Hybrid silica membranes, 150kPa steam, 200°C, total period of 300h.	H <sub>2</sub> /CO <sub>2</sub> permselectivities (>700)	[83]
H <sub>2</sub> permeation and recovery from H <sub>2</sub> -N <sub>2</sub> mixture by using two Pd membranes	H <sub>2</sub> pressure differences ranged 1.0-4.0 atm. H <sub>2</sub> concentration in H <sub>2</sub> -N <sub>2</sub> ranged 50-100 vol%. Membrane temperature ranged 320-380°C.	Permeance of 0.0220.359. >46% H <sub>2</sub> is recovered. No less than 65%, at least 92% of H <sub>2</sub> can be recovered from the feed gas.	[84]
CO <sub>2</sub> separation from flue gas by PP hollow fiber MC - no wetting	PP membrane contactor was operated for 40h.	CO <sub>2</sub> removal efficiency about 90% by using aqueous PG solution.	[85]
CO <sub>2</sub> separation by capillary transport membrane	Gas CO <sub>2</sub> and N <sub>2</sub> . Feed: atm pressure, permeate: 9-27 kPa.	76% CO <sub>2</sub> recovery, 99.8% purity. The selectivity of CO <sub>2</sub> /N <sub>2</sub> from about 800 to 8000.	[77]
CO <sub>2</sub> separation in Integrated Gasification Combined Cycle	Flue gas, CO <sub>2</sub> 36.4%, H <sub>2</sub> 56.8%, up to 400°C	85% H <sub>2</sub> recovery	[86]
SPEEK membrane for	CO <sub>2</sub> /CH <sub>4</sub> (30% CO <sub>2</sub> ) and CO <sub>2</sub> /N <sub>2</sub> (10% CO <sub>2</sub> ). Gas	Selectivity of CO <sub>2</sub> /CH <sub>4</sub> and CO <sub>2</sub> /N <sub>2</sub> were 56.8	[87]

CO <sub>2</sub> separation	test at 30 °C and 1.5 bar	and 62.0 respectively	
Polybenzoxazole membranes for CO <sub>2</sub> /N <sub>2</sub> separation	Mixed gas 15 mol% CO <sub>2</sub> , 75 mol% N <sub>2</sub> . Feed pressure from 1 to 6 bar at 25 °C	CO <sub>2</sub> permeance of 2500GPU and CO <sub>2</sub> /N <sub>2</sub> ideal selectivity of 16	[88]
CO <sub>2</sub> separation using thermally rearranged membranes	Mixed gas (CO <sub>2</sub> :N <sub>2</sub> :O <sub>2</sub> =15:80:5) for temperature range of 25–75 °C	CO <sub>2</sub> /N <sub>2</sub> selectivity of 20 at 25 °C at dry condition. CO <sub>2</sub> /N <sub>2</sub> selectivity of 16 at 25 °C for wet condition	[89]
Sod-ZMOF/ Matrimids MMMs for CO <sub>2</sub> separation	Mixed gas 50:50 mol%CO <sub>2</sub> /CH <sub>4</sub>	The best CO <sub>2</sub> permeability and CO <sub>2</sub> /CH <sub>4</sub> selectivity (13.79 barrer and 43.4)	[90]
Mg-MOF-74/CPO-27-Mg membrane for H <sub>2</sub> /CO <sub>2</sub> separation	Mixed gas 50 ml min <sup>-1</sup> H <sub>2</sub> , 50 ml min <sup>-1</sup> CO <sub>2</sub> , N <sub>2</sub> as sweep gas 50 ml min <sup>-1</sup> , 1 bar, 25 °C	H <sub>2</sub> permeability 2.5 x 10 <sup>3</sup> barrer H <sub>2</sub> /CO <sub>2</sub> selectivity 28	[91]
PVA polysiloxane/ silica membranes with amines for CO <sub>2</sub> /H <sub>2</sub> separation	Mixed gas 20% CO <sub>2</sub> and 80% H <sub>2</sub> flow rate 165cm <sup>3</sup> /min respectively. Ar as sweep gas 30cm <sup>3</sup> /min, 107 °C and 220 psia	Membrane with 22.3 wt% FS loading; CO <sub>2</sub> /H <sub>2</sub> selectivity 87 CO <sub>2</sub> permeability 1296 barrer	[92]

Based on the findings discussed, it can be concluded that the separation of mixed gases for various gas components such as H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and others can be done using absorption, adsorption, and membrane techniques. Each technique has its own advantages and disadvantages, depending on the type of solvent, absorbent, or membrane materials, as well as the separation conditions, which include temperature, pressure, flow rate, and other parameters. Gas upgrading using PVA and PSA shows that the highest recovery could be achieved by You et al. [44] with 99.99% H<sub>2</sub> purity and 80% recovery (Table 4). The separation of gases from H<sub>2</sub> and CO<sub>2</sub> in a membrane with a selectivity of 27.28 at a temperature of 400°C using PBI hollow-fiber membranes was recorded by Kumbharkar et al. [66]. Whereas, Blinova et al. [78] found that the CO<sub>2</sub> permeability over CH<sub>4</sub> is 3460 with a selectivity of 540 for a feed gas of 90% CH<sub>4</sub>/10% CO<sub>2</sub> at 128 kPa using functionalized polyaniline (PANI)-based composite membranes. These findings could lead to the application of this technique in real-scale industrial applications for gas separation, especially for the separation of CO<sub>2</sub> and H<sub>2</sub> using the different techniques mentioned.

## 2.4. Current status of gas separation using different separation techniques

Separation and/or removal of CO<sub>2</sub> in order to purify biogas [34], biohydrogen [60], and other gases [78] using the membrane technology has been repeatedly reported. Sufficient information could also be obtained for separating CO<sub>2</sub> from the mixed gases using PSA and PVA techniques [25]. The advantages and disadvantages of different techniques for the separation and/or removal of CO<sub>2</sub> from gas mixtures

(mainly CH<sub>4</sub> here) are presented in Table 6. Based on the findings in Table 6, it can be concluded that chemical absorption with amines is likely to be the best technique for CO<sub>2</sub> removal, as it gave the highest efficiency with more than 99% CH<sub>4</sub> purities and very low CH<sub>4</sub> losses. However, absorption using amines such as MEA, DEA, and MDEA could bring several drawbacks such as corrosion to the system, decomposition and poisoning of the amines by O<sub>2</sub> or other chemicals [34], high solution circulation rate and solution degradation [93].

**Table 6. Advantages and disadvantages of gas upgrading techniques for CO<sub>2</sub> removal from biogas mixture [34].**

Upgrading	Advantages	Disadvantages
<b>Absorption with water</b>	<ul style="list-style-type: none"> <li>• High efficiency (&gt; 97% CH<sub>4</sub>)</li> <li>• Simultaneous removal of H<sub>2</sub>S when H<sub>2</sub>S &lt; 300 cm<sup>3</sup>m<sup>-3</sup></li> <li>• Easy in operation</li> <li>• Capacity is adjustable by changing pressure or temperature</li> <li>• Possible regeneration</li> <li>• Low CH<sub>4</sub> losses (&lt;2%)</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive investment</li> <li>• Expensive operation</li> <li>• Clogging due to bacterial growth</li> <li>• Possible foaming</li> <li>• Less flexible towards variation of input gas</li> </ul>
<b>Chemical absorption with amines</b>	<ul style="list-style-type: none"> <li>• High efficiency (&gt;99% CH<sub>4</sub>)</li> <li>• Cheap operation</li> <li>• Regenerative</li> <li>• More CO<sub>2</sub> dissolved per unit of volume (compared to water)</li> <li>• Very low CH<sub>4</sub> losses (&lt;0.1%)</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive investment</li> <li>• Heat required for regeneration</li> <li>• Corrosion</li> <li>• Decomposition and poisoning of the amines by O<sub>2</sub> or other chemicals</li> <li>• Precipitation of salts</li> <li>• Foaming possible</li> </ul>
<b>Adsorption (PSA/VSA)</b>	<ul style="list-style-type: none"> <li>• Highly efficient (95-98% CH<sub>4</sub>)</li> <li>• H<sub>2</sub>S is removed</li> <li>• Low energy use: high pressure, but regenerative</li> <li>• Compact technique</li> <li>• Also for small capacities</li> <li>• Tolerant to impurities</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive investment</li> <li>• Expensive operation</li> <li>• Extensive process control needed</li> <li>• CH<sub>4</sub> losses when malfunctioning of valves</li> </ul>
<b>Membrane technology</b>	<ul style="list-style-type: none"> <li>• H<sub>2</sub>S and H<sub>2</sub>O are removed</li> </ul>	<ul style="list-style-type: none"> <li>• Low membrane selectivity: compromise between purity of CH<sub>4</sub> and amount of upgraded biogas</li> </ul>
<b>Gas/gas</b>	<ul style="list-style-type: none"> <li>• Simple construction</li> </ul>	<ul style="list-style-type: none"> <li>• Multiple steps required (modular system) to reach high purity CH<sub>4</sub> losses</li> </ul>
<b>a) Membrane for gas permeation</b>	<ul style="list-style-type: none"> <li>• Simple operation</li> </ul>	
<b>Gas/liquid A</b>	<ul style="list-style-type: none"> <li>• High reliability</li> </ul>	
<b>a) Membrane</b>	<ul style="list-style-type: none"> <li>• Small gas flows treated without</li> </ul>	

<b>Contactor</b>	proportional	• Little operational experience
<b>b) Supported Liquid Membranes (SLMs)</b>	<ul style="list-style-type: none"> <li>• increase of costs</li> <li>Gas/gas</li> <li>• Removal efficiency:</li> <li>• &lt;92% CH<sub>4</sub> (1 step) or &gt; 96% CH<sub>4</sub></li> <li>• H<sub>2</sub>O is removed</li> <li>Gas/liquid</li> <li>• Removal efficiency: &gt; 96% CH<sub>4</sub></li> <li>• Cheap investment and operation</li> <li>• Pure CO<sub>2</sub> can be obtained</li> </ul>	

Adsorption on the other hand brings a huge potential for CO<sub>2</sub> from gas mixtures with high efficient (95-98% CH<sub>4</sub>). However, adsorption would require high cost of investment, operation and process control which leads to the finding of new potential technology for better separation and purification in near future. Membrane technology currently shows a good potential but the application is still limited and require more operational experience in real industry.

### 3. Energy, Economy and Environmental aspects for Gas-Separation Techniques

In determining the suitability of a gas-separation/-upgrading technique to be applied in real- or industrial-scale application, there are several aspects that have to be considered, namely energy, economy, and environmental concerns. Andriani et al. [94] reviewed a few gas-upgrading techniques and reported the aspects of energy and economy that may influence it. Energy aspects refer to the energy requirements for the operation of each technique, whereas the economy aspects include general data related to the investment and operating costs for each technique [95]. A summary of the energy requirements as well as the technical and involved costs for each of the separation techniques are presented in Tables 7 and 8, respectively. In general, both tables give the overall data for the individual aspects of each technique that should be taken into consideration in evaluating gas-separation technology. This technology consists of water scrubbing, chemical scrubbing, PSA, and membrane technique.

Table 7 summarizes the energy requirements for absorption, adsorption, and membrane techniques, as reported by Andriani et al. [94]. Based on Table 7, Persson [96] reported that the lowest energy requirement for the biogas-upgrading technique was using chemical scrubbing with a value of 0.15 kWh/m<sup>3</sup> for the upgraded biogas. However, no energy value has been reported for using the membrane technique. The lowest energy requirement reported by Beil [97] is similar to that of Persson [96], which used a chemical scrubbing technique with 0.12 kWh/m<sup>3</sup> for the upgraded biogas, whereas the PSA technique showed the highest energy requirement with 0.24 kWh/m<sup>3</sup> for the upgraded biogas.

Apart from the separation efficiency and energy requirement for each of the technology presented, further key factors that can be used to determine the

suitability of the biogas-upgrading technique include the technical availability per year, maintenance costs, and the estimated cost per m<sup>3</sup> associated with the upgrading technologies for a 1000 m<sup>3</sup>/h of raw biogas-upgrading plant [98]. Table 8 summarizes all available data for the commonly known technologies for gas upgrading based on the report by Beil [97]. The highest technical availability per year (98%) was identified using a membrane technique, which was followed by water scrubbing (96%), PSA (94%), and lastly chemical scrubbing (91%) [97]. Water scrubbing is the one that requires less maintenance costs among the other techniques with 15,000 €/yr compared to chemical scrubbing and PSA that can be associated with costs more than three times that. The highest cost per m<sup>3</sup> for an upgrading technique was determined to be the PSA technique with 0.26 €/m<sup>3</sup>. Overall, water scrubbing has the lowest costs for maintenance per m<sup>3</sup>, with lower technical availability than membrane techniques. Membrane techniques, on the other hand, possess an average-level maintenance cost and cost per m<sup>3</sup> compared to the rest, but they have the highest technical availability.

**Table 7. Energy requirements for different biogas upgrading techniques [94].**

<b>Techniques</b>	<b>Energy requirement (kWh/m<sup>3</sup> of upgraded biogas)</b>	
	[96]	[97]
<b>Water absorption</b>	0.3	0.2
<b>Chemical absorption</b>	0.15	0.12
<b>Pressure swing adsorption</b>	0.5-0.6	0.24
<b>Membrane</b>	-	0.19

The next important aspect commonly considered for gas upgrading is the environmental aspect, which is indicated by the level of methane loss associated with a chosen gas-upgrading technique. Any methane lost during the process does not only represent a loss of revenue, but also a significant contributor to climate change, as methane has the potential to lead to the occurrence of global warming [95]. Table 9 summarizes the environmental aspects for gas-separation techniques, as reported by Niesner et al. [95]. The main consideration for selecting specific techniques is the amount of energy required to upgrade the raw biogas to biohydrogen. It is crucial to ensure that the energy consumption is as low as possible so that more net energy is available for the end use [98]. Methane losses (as a percentage) associated with gas-upgrading techniques were summarized by Niesner et al. [95] based on different literature sources [99-101]. All of the sources confirmed that chemical scrubbing gives the lowest methane losses, whereas the highest is given by the membrane technique. Water scrubbing and PSA give intermediate losses (%). All sources reported a similar pattern in terms of methane losses, but it is still limited and more research needs to be carried out.

Based on all of the techniques presented, the absorption technique (water/chemical scrubbing) clearly has the best performance in terms of energy requirement, cost, and environmental aspects. Niesner et al. [95] revealed that the most favored biogas-upgrading technology in the European region is water absorption, followed by PSA and chemical scrubbing. Water scrubbing/absorption are proven to be used in real applications, as it involves a simple process and is universally applicable for various flow rates. The absorption technology seems to be well established, but is conventional [95]. Of all the technologies we are

focusing on, PSA and membrane techniques could offer various potentials, as they are currently used for medium- or large-scale plants only.

**Table 8. The technical availability per year, maintenance cost and estimated cost per m<sup>3</sup> for different gas upgrading techniques [97].**

Gas Upgrading Techniques	Technical availability per year (%)	Maintenance Cost (€/yr) (*RM/yr)	Cost per m <sup>3</sup> (€/m <sup>3</sup> )	(*RM/m <sup>3</sup> )	(*RM/yr)
Water scrubbing	96	15000	63000	0.15	0.63
Chemical scrubbing	91	59000	250000	-	-
Pressure swing adsorption	94	56000	240000	0.26	1.09
Membrane	98	25000	110000	0.22	0.92

\*The cost in RM is based on the latest currency exchange from € of 1€=RM4.18

**Table 9. Summary of methane losses associated with different biogas upgrading techniques [95].**

Techniques	Methane losses (%)		
	[99]	[101]	[100]
Water scrubbing	Medium	4.7	<2
Chemical scrubbing	Low	0.03	<0.1
Pressure swing adsorption	medium	5.5	2
Membrane	high	-	>10

#### 4. Potential Biogas-Upgrading Technique for Palm Oil Mill

It has previously been found that the chemical scrubbing technique has the lowest energy requirement, with 0.12 kWh/m<sup>3</sup> for upgrading biogas compared to membrane and water-scrubbing techniques, which require 0.19 and 0.2 kWh/m<sup>3</sup>, respectively (Table 5). On the other hand, the membrane technique has the highest technical availability of 98%, which is followed by water scrubbing with 94% (Table 7). However, water scrubbing brings the lowest maintenance cost of 15,000 €/year and a cost per m<sup>3</sup> of 0.15 €/m<sup>3</sup> (Table 8). According to the summaries in Tables 7 to 9 in Section 3, the performance criteria for all commonly chosen techniques are presented in Table 10. A scoring system is introduced, using the Likert scales method to find the best technique for gas upgrading after considering various factors. This method is a non-comparative scaling technique and is unidimensional, where it only measures a single trait. Generally, the Likert scales use a 5-point scale, whereas some practitioners advocate the use of 7 to 9-point scales, which add additional granularity. However, sometimes a 4-point scale is used to produce a forced choice, where no indifferent option is available. Each level on the scale is assigned a numeric value or coding, usually starting at 1 and incremented by one for each level [102].

According to Table 10, it can be observed that the highest total score is owned by water scrubbing, with score of 16, followed by membrane, chemical scrubbing and finally PSA, with scores of 14, 11, and 9, respectively. Therefore, it can be concluded that water scrubbing is found to be the best technique to be used in the

industry. This is followed by membrane scrubbing, chemical scrubbing, and PSA based on the highest total score obtained. Hence, water scrubbing is the most potential technique to be applied for upgrading the biohydrogen from oil mill effluent by taking into consideration to this finding.

**Table 10. Different performances criteria for well-known gas upgrading techniques identified by using Likert scale.**

Technique	Performance Criteria					Total
	Energy Requirement	Technical availability	Maintenance cost	Cost per m <sup>3</sup>	Methane losses	
Water absorption	2	3	4	4	3	16
Chemical absorption	4	1	1	1	4	11
Pressure swing adsorption	1	2	2	2	2	9
Membrane	3	4	3	3	1	14

Rank: 1 is the worst and 4 is the best following Likert Scale

## 5. Concluding Remarks

Treatment of POME is crucial as it possesses a high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) with 100 times more than domestic sewage, a high solids concentration, and it is highly acidic, makes the effluent to be highly polluting POME treatment through aerobic digestions may produce mixed gases (methane/CO<sub>2</sub> and biohydrogen/CO<sub>2</sub>) that could be used to work towards a greener environment upon upgrading.

Various gas-separation techniques have been developed and presented in this review. A technique can be chosen based on several aspects, which include the energy, economy, and environmental aspects. Commonly chosen techniques include water/chemical scrubbing, PSA, and membrane techniques. Based on these criteria and review, water scrubbing is found to be the best technique to be used in the biogas-upgrading industry, followed by membrane and chemical scrubbing as well as PSA. Hence, these guidelines are justified for selecting the best gas-upgrading technique to be used in palm oil mill industry applications.

## Acknowledgements

The authors gratefully acknowledge Kursi UKM – YSD for financial support of the project PKT 6/2012 and Universiti Kebangsaan Malaysia for the research grant of GUP-2016-086.

## References

1. Ji, C.M.; Eong, P.P.; Ti, T.B.; Seng, C.E.; Ling, C.K. (2013). Biogas from palm oil mill effluent (POME): Opportunities and challenges from Malaysia's perspective. *Renewable and Sustainable Energy Reviews*, 26, 717-726.
2. Mumtaz, T.; Yahaya, N.A.; Abd-Aziz, S.; Rahman, N.A.A.; Yee, P.L.; Shirai, Y.; Hassan, M.A. (2010). Turning waste to wealth-biodegradable plastics

- polyhydroxyalkanoates from palm oil mill effluent – a Malaysian perspective. *Journal of Cleaner Production*, 18(14), 1393-1402.
- 3. Awalludin, M.F.; Sulaiman, O.; Hashim, R.; Nadhari, W.N.A.W. (2015). An overview of the oil palm industry in Malaysia and its waste utilization through thermochemical conversion, specifically via liquefaction. *Renewable and Sustainable Energy Reviews*, 50, sa1469-1484.
  - 4. Sulaiman, F.; Abdullah, N.; Gerhauser, H.; Shariff, A. (2011). An outlook of Malaysian energy, oil palm industry and its utilization of wastes as useful resources. *Biomass and Bioenergy*, 35(9):3775-3786
  - 5. Abdurahman, N.H.; Rosli, Y.M.; Azhari, N.H. (2011). Development of a membrane anaerobic system (MAS) for palm oil mill effluent (POME) treatment. *Desalination*, 266 (1-3), 208-212.
  - 6. Zahrim, A.Y.; Nasimah, A.; Hilal, N. (2014). Pollutants analysis during conventional palm oil mill effluent (POME) ponding system and decolourisation of anaerobically treated POME via calcium lactate-polyacrylamide. *Journal of Water Process Engineering*, 4, 159-165.
  - 7. Chan, Y.J.; Tan, W.J.R.; How, B.S.; Lee, J.J.; Lau, V.Y. (2015). Fuzzy optimisation approach on the treatment of palm oil mill effluent (POME) via up-flow anaerobic sludge blanket–hollow centered packed bed (UASB–HCPB) reactor. *Journal of Water Process Engineering*, 5, 112-117.
  - 8. Parthasarathy, S.; Mohammed, R.R.; Fong, C.M.; Gomes, R.L.; Manickam, S. (2015). A novel hybrid approach of activated carbon and ultrasound cavitation for the intensification of palm oil mill effluent (POME) polishing. *Journal of Cleaner Production*, 112, 1218-1226.
  - 9. Lam, M.K.; and Lee, K.T. (2011). Renewable and sustainable bioenergies production from palm oil mill effluent (POME): win-win strategies toward better environmental protection. *Biotechnology advances*, 29(1), 124-141.
  - 10. Wu, T.Y.; Mohammad, A.W.; Jahim, J.M.; Anuar, N. (2009). A holistic approach to managing palm oil mill effluent (POME): biotechnological advances in the sustainable reuse of POME. *Biotechnology advances*, 27(1), 40-5211.
  - 11. Kling, S. (2007). *Determination of domestic waste water characteristics and its relation to the type and size of developments*. Universiti Teknologi Malaysia.
  - 12. Council EQ .(2009). Environmental Quality (Sewage) Regulations 2009. In: PU(A) 432/2009.
  - 13. Ahmed, Y.; Yaakob, Z.; Akhtar, P.; Sopian, K. (2015). Production of biogas and performance evaluation of existing treatment processes in palm oil mill effluent (POME). *Renewable and Sustainable Energy Reviews*, 42, 1260-1278.
  - 14. Wu, T.Y.; Mohammad, A.W.; Jahim, J.M.; Anuar, N. (2010). Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. *Journal of environmental management*, 91(7), 1467-1490.
  - 15. Harsono, S.S.; Grundmann, P.; Soebronto, S. (2014). Anaerobic treatment of palm oil mill effluents: potential contribution to net energy yield and reduction of greenhouse gas emissions from biodiesel production. *Journal of Cleaner Production*, 64, 619-627.

16. Poh, P.E.; and Chong, M.F. (2010). Biomethanation of Palm Oil Mill Effluent (POME) with a thermophilic mixed culture cultivated using POME as a substrate. *Chemical Engineering Journal*, 164(1), 146-154.
17. Ismail, I.; Hassan, M.A.; Abdul Rahman, N.A.; Soon, C.S. (2010). Thermophilic biohydrogen production from palm oil mill effluent (POME) using suspended mixed culture. *Biomass and Bioenergy*, 34(1), 42-47.
18. Sayari, A.; Belmabkhout, Y.; Serna-Guerrero, R. (2011). Flue gas treatment via CO<sub>2</sub> adsorption. *Chemical Engineering Journal*, 171(3), 760-774.
19. Hongjun, Y.; Shuansi, F.; Xuemei, L.; Yanhong, W.; Jinghua, N. (2011). Economic Comparison of Three Gas Separation Technologies for CO<sub>2</sub> Capture from Power Plant Flue Gas. *Chinese Journal of Chemical Engineering*, 19(4), 615-620.
20. Kim, K.H.; Ingole, P.G.; Kim, J.H.; Lee, H.K. (2013). Separation performance of PEBAK/PEI hollow fiber composite membrane for SO<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> mixed gas. *Chemical Engineering Journal*, 233, 242-250.
21. Rufford, T.E.; Smart, S.; Watson, G.C.Y.; Graham, B.F.; Boxall, J.; Diniz da Costa, J.C.; May, E.F. (2012). The removal of CO<sub>2</sub> and N<sub>2</sub> from natural gas: A review of conventional and emerging process technologies. *Journal of Petroleum Science and Engineering*, 94-95, 123-154.
22. Bakonyi, P.; Nemestóthy, N.; Bélafi-Bakó, K. (2013). Biohydrogen purification by membranes: An overview on the operational conditions affecting the performance of non-porous, polymeric and ionic liquid based gas separation membranes. *International Journal of Hydrogen Energy*, 38(23), 9673-9687.
23. Nemestóthy, N.; Bakonyi, P.; Tóth, G.; K. B-B. (2012). Feasibility study of gas separation membranes for biohydrogen separation. *Procedia Engineering*, 44, 976-979.
24. Abanades, J.C.; Arias, B.; Lyngfelt, A.; Mattisson, T.; Wiley, D.E.; Li, H.; Ho, M.T.; Mangano, E.; Brandani, S. (2015). Emerging CO<sub>2</sub> capture systems. *International Journal of Greenhouse Gas Control*, 40, 126-166.
25. Moon, S.H.; and Shim, J.W. (2006). A novel process for CO<sub>2</sub>/CH<sub>4</sub> gas separation on activated carbon fibers electric swing adsorption. *Journal of Colloid and Interface Science*, 298(2), 523-528.
26. Delgado, J.A.; Uguina, M.A.; Sotelo, J.L.; Ruíz, B.; Rosário, M. (2007). Carbon dioxide/methane separation by adsorption on sepiolite. *Journal of Natural Gas Chemistry*, 16(3), 235-243.
27. Dasgupta, S.; Biswas, N.; Aarti, Gode, N.G.; Divekar, S.; Nanoti, A.; Goswami, A.N. (2012). CO<sub>2</sub> recovery from mixtures with nitrogen in a vacuum swing adsorber using metal organic framework adsorbent: A comparative study. *International Journal of Greenhouse Gas Control*, 7, 225-229.
28. Plaza, M.G.G.S.; Rubiera, F.; Pis, J.J.; Pevida, C. (2011). Evaluation of ammonia modified and conventionally activated biomass based carbons as CO<sub>2</sub> adsorbents in postcombustion conditions. *Separation and Purification Technology*, 80(1), 96-104.
29. Zhang, J.; Webley, P.A.; Xiao, P. (2008). Effect of process parameters on power requirements of vacuum swing adsorption technology for CO<sub>2</sub> capture from flue gas. *Energy Conversion and Management*, 49(2), 346-356.

30. Badiei, M.; Jahim, J.M.; Anuar, N.; Sheikh Abdullah, S.R. (2011). Effect of hydraulic retention time on biohydrogen production from palm oil mill effluent in anaerobic sequencing batch reactor. *International Journal of Hydrogen Energy*, 36(10), 5912-5919.
31. Spigarelli, B.P.; Kawatra, S.K. (2013). Opportunities and challenges in carbon dioxide capture. *Journal of CO<sub>2</sub> Utilization*, 1, 69-87.
32. Tan, J.; Lu, Y.C.; Xu, J.H.; Luo, G.S. (2013). Modeling investigation of mass transfer of gas-liquid concurrent flow processes. *Separation and Purification Technology*, 109, 77-86.
33. Pires, J.C.M.; Martins, F.G.; Alvim-Ferraz, M.C.M.; Simões, M. (2011). Recent developments on carbon capture and storage: An overview. *Chemical Engineering Research and Design*, 89(9), 1446-1460.
34. Ryckebosch, E.; Drouillon, M.; Vervaeren, H. (2011). Techniques for transformation of biogas to biomethane. *Biomass and Bioenergy*, 35(5), 1633-1645.
35. Yeo, Z.Y.; Chew, T.L.; Zhu, P.; Mohamed, A.R.; Chai, S-P. (2012). Conventional processes and membrane technology for carbon dioxide removal from natural gas: A review. *Journal of Natural Gas Chemistry*, 21(3), 282-298.
36. Tepe, J.B.; Dodge, B.F. (1943). Absorption of carbon dioxide by sodium hydroxide solutions in a packed column. *Trans Am Inst Chem Eng*, 39, 255-276.
37. Spector, N.; Dodge, B. (1946). Removal of carbon dioxide from atmospheric air. *Trans Am Inst Chem Eng*, 42, 827-848.
38. Yoo, M.; Han, S.J.; Wee, J.H. (2013). Carbon dioxide capture capacity of sodium hydroxide aqueous solution. *Journal of environmental management*, 114, 512-519.
39. Ma, S.; Song, H.; Wang, M.; Yang, J.; Zang, B. (2013). Research on mechanism of ammonia escaping and control in the process of CO<sub>2</sub> capture using ammonia solution. *Chemical Engineering Research and Design*, 91(7), 1327-1334.
40. Yeo, T.H.C.; Tan, I.A.W.; Abdullah, M.O. (2012). Development of adsorption air-conditioning technology using modified activated carbon – A review. *Renewable and Sustainable Energy Reviews*, 16(5), 3355-3363.
41. Sen, Gupta. S.; Bhattacharyya, K.G. (2011). Kinetics of adsorption of metal ions on inorganic materials: A review. *Advances in Colloid and Interface Science*, 162(1-2), 39-58.
42. Hedin, N.; Andersson, L.; Bergström, L.; Yan, J. (2013). Adsorbents for the post-combustion capture of CO<sub>2</sub> using rapid temperature swing or vacuum swing adsorption. *Applied Energy*, 104, 418-433.
43. Nikolic, D.; Giovanoglou, A.; Georgiadis, M.C.; Kikkinides, E.S. (2007). Hydrogen purification by pressure swing adsorption. *Proceedings of the 10<sup>th</sup> conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction (PRES) 2007*, At Ischia, Gulf of Naples, Italy.
44. You, Y.-W.; Lee, D.-G.; Yoon, K.-Y.; Moon, D.-K.; Kim, S.M.; Lee, C.-H. (2012). H<sub>2</sub> PSA purifier for CO removal from hydrogen mixtures. *International Journal of Hydrogen Energy*, 37(23), 18175-18186.

45. Montanari, T.; Finocchio, E.; Salvatore, E.; Garuti, G.; Giordano, A.; Pistarino, C.; Busca, G. (2011). CO<sub>2</sub> separation and landfill biogas upgrading: A comparison of 4A and 13X zeolite adsorbents. *Energy*, 36(1), 314-319.
46. Grande, C.A.; Ribeiro, R.P.L.; Oliveira, E.L.G.; Rodrigues, A.E. (2009). Electric swing adsorption as emerging CO<sub>2</sub> capture technique. *Energy Procedia*, 1(1), 1219-1225.
47. Liu, Z.; Grande, C.A.; Li, P.; Yu, J.; Rodrigues, A.E. (2011). Multi-bed vacuum pressure swing adsorption for carbon dioxide capture from flue gas. *Separation and Purification Technology*, 81(3), 307-317.
48. Lopes, FVS.; Grande, C.A.; Rodrigues, A.E. (2011). Activated carbon for hydrogen purification by pressure swing adsorption: Multicomponent breakthrough curves and PSA performance. *Chemical Engineering Science*, 66(3), 303-317.
49. Ahn, S.; You, Y-W.; Lee, D-G.; Kim, K-H.; Oh, M.; Lee, C-H. (2012). Layered two- and four-bed PSA processes for H<sub>2</sub> recovery from coal gas. *Chemical Engineering Science*, 68(1), 413-423.
50. Huang, Q.; Eić, M. (2013). Commercial adsorbents as benchmark materials for separation of carbon dioxide and nitrogen by vacuum swing adsorption process. *Separation and Purification Technology*, 103, 203-215.
51. Maring, B.J.; and Webley, P.A. (2013). A new simplified pressure/vacuum swing adsorption model for rapid adsorbent screening for CO<sub>2</sub> capture applications. *International Journal of Greenhouse Gas Control*, 15, 16-31.
52. Casas, N.; Schell, J.; Joss, L.; Mazzotti, M. (2013). A parametric study of a PSA process for pre-combustion CO<sub>2</sub> capture. *Separation and Purification Technology*, 104, 183-192.
53. Su, F.; Lu, C.; Chung, A-J.; Liao, C-H. (2014). CO<sub>2</sub> capture with amine-loaded carbon nanotubes via a dual-column temperature/vacuum swing adsorption. *Applied Energy*, 113, 706-712.
54. García, S.; Martín, C.F.; Pis, J.J.; Rubiera, F.; Pevida, C. (2013). Dynamic cyclic performance of phenol-formaldehyde resin-derived carbons for pre-combustion CO<sub>2</sub> capture: An experimental study. *Energy Procedia*, 37, 127-133.
55. Riboldi, L.; Bolland, O.; Ngoy, J.M.; Wagner, N. (2014). Full-plant analysis of a PSA CO<sub>2</sub> capture unit integrated in coal-fired power plants: post-and pre-combustion scenarios. *Energy Procedia*, 63, 2289-2304.
56. Casas, N.; Schell, J.; Blom, R.; Mazzotti, M. (2013). MOF and UiO-67/MCM-41 adsorbents for pre-combustion CO<sub>2</sub> capture by PSA: Breakthrough experiments and process design. *Separation and Purification Technology*, 112, 34-48.
57. Adewole, J.K.; Ahmad, A.L.; Ismail, S.; Leo, C.P. (2013). Current challenges in membrane separation of CO<sub>2</sub> from natural gas: A review. *International Journal of Greenhouse Gas Control*, 17, 46-65.
58. Scholes, C.A.; Kentish, S.E.; Stevens, G.W. (2008). Carbon dioxide separation through polymeric membrane systems for flue gas applications. In: *Recent Patents on Chemical Engineering*. vol. 1, 52-66.
59. Yildirim, Y.; and Hughes, R. (2003). An experimental study of CO<sub>2</sub> separation using a silica based composite membrane. *Process Safety and Environmental Protection*, 81(4), 257-261.

60. Modigell, M.; Schumacher, M.V.; Teplyakov, V.; Zenkevich, V.B. (2008). A membrane contactor for efficient CO<sub>2</sub> removal in biohydrogen production. *Desalination*, 224(1-3), 186-190.
61. Beggel, F.; Nowik, I.J.; Modigell, M.; Shalygin, M.G.; Teplyakov, V.V.; Zenkevitch, V.B. (2010). A novel gas purification system for biologically produced gases. *Journal of Cleaner Production*, 18, S43-S50.
62. Rangou, S.; Shishatskiy, S.; Filiz, V.; Abetz, V. (2011). Poly(vinyl trimethylsilane) and block copolymers of vinyl trimethylsilane with isoprene: Anionic polymerization, morphology and gas transport properties. *European Polymer Journal*, 47, 723-729.
63. Shalygin, M.G.; Roizard, D.; Favre, E.; Teplyakov, V.V. (2008). CO<sub>2</sub> transfer in an aqueous potassium carbonate liquid membrane module with dense polymeric supporting layers: Influence of concentration, circulation flow rate and temperature. *Journal of Membrane Science*, 318(1-2), 317-326.
64. Luis, P.; Van Gerven, T.; Van der Bruggen, B. (2012). Recent developments in membrane-based technologies for CO<sub>2</sub> capture. *Progress in Energy and Combustion Science*, 38(3), 419-448.
65. Mondal, M.K.; Balsora, H.K.; Varshney, P. (2010). Progress and trends in CO<sub>2</sub> capture/separation technologies: A review. *Energy*, 46(1), 431-441.
66. Kumbharkar, S.C.; Liu, Y.; Li, K. (2011). High performance polybenzimidazole based asymmetric hollow fibre membranes for H<sub>2</sub>/CO<sub>2</sub> separation. *Journal of Membrane Science*, 375(1-2), 231-240.
67. Yingying, J.; Youting, W.; Wenting, W.; Lei, L.; Zheng, Z.; Zhibing, Z. (2009). Permeability and selectivity of sulfur dioxide and carbon dioxide in supported ionic liquid membranes. *Chinese Journal of Chemical Engineering*, 4(17), 594-601.
68. De los Ríos, A.P.; Hernández-Fernández, F.J.; Lozano, L.J.; Sánchez-Segado, S.; Ginestá-Anzola, A.; Godínez, C.; Tomás-Alonso, F.; Quesada-Medina, J. (2013). On the selective separation of metal ions from hydrochloride aqueous solution by pertraction through supported ionic liquid membranes. *Journal of Membrane Science*, 444, 469-481.
69. Neves, L.A.; Crespo, J.G.; Coelhos, I.M. (2010). Gas permeation studies in supported ionic liquid membranes. *Journal of Membrane Science*, 357(1-2), 160-170.
70. Malik, M.A.; Hashim, M.A.; Nabi, F. (2011). Ionic liquids in supported liquid membrane technology. *Chemical Engineering Journal*, 171(1), 242-254.
71. Lozano, L.J.; Godínez, C.; De los Ríos, A.P.; Hernández-Fernández, F.J.; Sánchez-Segado, S.; Alguacil, F.J. (2011). Recent advances in supported ionic liquid membrane technology. *Journal of Membrane Science*, 376(1-2), 1-14.
72. Hernández-Fernández, F.J.; de los Ríos, A.P.; Tomás-Alonso, F.; Palacios, J.M.; Víllora, G. (2009). Preparation of supported ionic liquid membranes: Influence of the ionic liquid immobilization method on their operational stability. *Journal of Membrane Science*, 341(1-2), 172-177.
73. Myers, C.; Pennline, H.; Luebke, D.; Ilconich, J.; Dixon, J.K.; Maginn, E.J.; Brennecke, J.F. (2008). High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes. *Journal of Membrane Science*, 322(1), 28-31.

74. Hydrogen Efficiency Technologies. Retrieved June 30, 2015 from <http://www.hyet.nl/newsite/technology/working-principle>
75. Ströbel, R.; Oszcipok, M.; Fasil, M.; Rohland, B.; Jörissen, L.; Garche, J. (2002). The compression of hydrogen in an electrochemical cell based on a PE fuel cell design. *Journal of Power Sources*, 105, 208-215.
76. Grigoriev, S.A.; Djous, K.A.; Millet, P.; Kalinnikov, A.A.; Poremskiy, V.I.; Fateev, V.N.; Blach, R. (2008). Characterization of pem electrochemical hydrogen compressors. In. Hydrogen Energy and Plasma Technology Institute of Russian Research Center; 6.
77. Teramoto, M.; Kitada, S.; Ohnishi, N.; Matsuyama, H.; Matsumiya, N. (2004). Separation and concentration of CO<sub>2</sub> by capillary-type facilitated transport membrane module with permeation of carrier solution. *Journal of Membrane Science*, 234(1-2), 83-94.
78. Blinova, N.V.; and Svec, F. (2012). Functionalized polyaniline-based composite membranes with vastly improved performance for separation of carbon dioxide from methane. *Journal of Membrane Science*, 423-424, 514-521.
79. Smart, S.; Vente, J.F.; Diniz da Costa, J.C. (2012). High temperature H<sub>2</sub>/CO<sub>2</sub> separation using cobalt oxide silica membranes. *International Journal of Hydrogen Energy*, 37(17), 12700-12707.
80. Sandström, L.; Sjöberg, E.; Hedlund, J. (2011). Very high flux MFI membrane for CO<sub>2</sub> separation. *Journal of Membrane Science*, 380(1-2), 232-240.
81. Ramírez-Morales, J.E.; Tapia-Venegas, E.; Nemestóthy, N.; Bakonyi, P.; Be'lafi-Bako', K.; Ruiz-Filippi, G. (2013). Evaluation of two gas membrane modules for fermentative hydrogen separation. *International Journal of Hydrogen Energy*, 38(32), 14042-14052.
82. Ji, G.; Wang, G.; Hooman, K.; Bhatia, S.; Costa, J.C.D.d. (2013). Simulation of binary gas separation through multi-tube molecular sieving membranes at high temperatures. *Chemical Engineering Journal*, 218, 394-404.
83. Qi, H.; Chen, H.; Li, L.; Zhu, G.; Xu, N. (2012). Effect of Nb content on hydrothermal stability of a novel ethylene-bridged silsesquioxane molecular sieving membrane for H<sub>2</sub>/CO<sub>2</sub> separation. *Journal of Membrane Science*, 421-422, 190-200.
84. Chen, W.-H.; Hsia, M.-H.; Lin, Y.-L.; Chi, Y.-H.; Yang, C.-C. (2013). Hydrogen permeation and recovery from H<sub>2</sub>-N<sub>2</sub> gas mixtures by Pd membranes with high permeance. *International Journal of Hydrogen Energy*, 38(34), 14730-14742.
85. Yan, S.-P.; Fang, M.-X.; Zhang, W.-F.; Wang, S.-Y.; Xu, Z.-K.; Luo, Z.-Y.; Cen, K.-F. (2007). Experimental study on the separation of CO<sub>2</sub> from flue gas using hollow fiber membrane contactors without wetting. *Fuel Processing Technology*, 88(5), 501-511.
86. Franz, J.; and Scherer, V. (2010). An evaluation of CO<sub>2</sub> and H<sub>2</sub> selective polymeric membranes for CO<sub>2</sub> separation in IGCC processes. *Journal of Membrane Science*, 359(1-2), 173-183.
87. Xin, Q.; Gao, Y.; Wu, X.; Li, C.; Liu, T.; Shi, Y.; Li, Y.; Jiang, Z.; Wu, H.; Cao, X. (2015). Incorporating one-dimensional aminated titania nanotubes into sulfonated poly(ether ether ketone) membrane to construct CO<sub>2</sub>-facilitated

- transport pathways for enhanced CO<sub>2</sub> separation. *Journal of Membrane Science*, 488, 13-29.
- 88. Woo, K.T.; Lee, J.; Dong, G.; Kim, J.S.; Do, Y.S.; Hung, W-S.; Lee, K-R.; Barbieri, G.; Drioli, E.; Lee, Y.M. (2015). Fabrication of thermally rearranged (TR) polybenzoxazole hollow fiber membranes with superior CO<sub>2</sub>/N<sub>2</sub> separation performance. *Journal of Membrane Science*, 490, 129-138.
  - 89. Cersosimo, M.; Brunetti, A.; Drioli, E.; Fiorino, F.; Dong, G.; Woo, K.T.; Lee, J.; Lee, Y.M.; Barbieri, G. (2015). Separation of CO<sub>2</sub> from humidified ternary gas mixtures using thermally rearranged polymeric membranes. *Journal of Membrane Science*, 492, 257-262.
  - 90. Kılıç, A.; Atalay-Oral, Ç.; Sirkecioğlu, A.; Tantekin-Ersolmaz, ŞB.; Ahunbay, MG. (2015). Sod-ZMOF/Matrimid® mixed matrix membranes for CO<sub>2</sub> separation. *Journal of Membrane Science*, 489, 81-89.
  - 91. Wang, N.; Mundstock, A.; Liu, Y.; Huang, A.; Caro, J. (2015). Amine-modified Mg-MOF-74/CPO-27-Mg membrane with enhanced H<sub>2</sub>/CO<sub>2</sub> separation. *Chemical Engineering Science*, 124, 27-36.
  - 92. Xing, R.; Ho, W.S.W. (2011). Crosslinked polyvinylalcohol-polysiloxane/fumed silica mixed matrix membranes containing amines for CO<sub>2</sub>/H<sub>2</sub> separation. *Journal of Membrane Science*, 367(1-2), 91-102.
  - 93. Liu, K.; Song, C.; Subramani, V. (2009). *Hydrogen and syngas production and purification technologies*. New Jersey: John Wiley and Sons.
  - 94. Andriani, D.; Wresta, A.; Atmaja, TD.; Saepudin, A. (2013). A review on optimization production and upgrading biogas through CO removal using various techniques. *Applied biochemistry and biotechnology*, 172 (4), 1909-1928.
  - 95. Niesner, J.; Jecha, D.; Stehlík, P. (2013). Biogas upgrading technologies: State of art review in European region. *Chemical Engineering Transactions*, 35, 517-522.
  - 96. Persson, M. (2017). Biogas upgrading and utilisation as a vehicle fuel. *Proceedings of the Future of Biogas in Europe III*, University of Southern Denmark.
  - 97. Beil, M. (2009). Overview on (biogas) upgrading technologies. In: *European Biomethane Fuel Conference*. vol. 09: Göteborg, Sweden.
  - 98. Patterson, T.; Esteves, S.; Dinsdale, R.; Guwy, A. (2011). An evaluation of the policy and techno-economic factors affecting the potential for biogas upgrading for transport fuel use in the UK. *Energy Policy*, 39(3), 1806-1816.
  - 99. CarboTech Engineering GmbH, Intelligent utilisation of biogas-upgrading and adding to the grid.Jonkoping,May 2006. Retrieved on April 5 2015 from [http://biogasinfo-board.de/pdf/presentation\\_CarboTech%20Engineering%20GmbH.pdf](http://biogasinfo-board.de/pdf/presentation_CarboTech%20Engineering%20GmbH.pdf)
  - 100. Biogas upgrading using the DMT Carborex PWS Technology, DMT Environmental Technology. Retrieved on April 15 2015 from [http://www.dirksmilieutechniek.com/dmt/do/download/\\_/true/210370/Biogas\\_upgrading\\_using\\_the\\_DMT\\_Carborex\\_PWS\\_\\_Technology.\\_2009.pdf](http://www.dirksmilieutechniek.com/dmt/do/download/_/true/210370/Biogas_upgrading_using_the_DMT_Carborex_PWS__Technology._2009.pdf)
  - 101. DGE GmbH Presentation: Purification of biomethane using pressureless purification for the production of biomethane and carbon dioxide. INNOGAS. Retrieved on June 30 2015 from <http://www.dge-wittenberg.com/english/vortraege/DGE%20Fachtagung%20WB%202006%20teil1-EN.pdf>
  - 102. Bertram D: Likert Scales. In.; 2007: 10. Retrieved on May 5 2015 from <http://www.topic-dane-likert.pdf>