

EVALUATION OF HYDROGEN PRODUCTION FROM CATALYTIC REFORMING OF LIQUEFIED PETROLEUM GAS WITH CARBON CAPTURE AND STORAGE

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ABSTRACT. The objective of this study was to describe the hydrogen production from catalytic reforming of liquefied petroleum gas (LPG) with carbon capture and storage (CCS). Nowadays, hydrogen requires a lot of attention as a clean fuel as well as a chemical used in industrial applications (e.g. hydrogenation processes especially in oil refinery sector). The size of evaluated plant was 100000 Nm³/h hydrogen with a purity of 99.95% (vol.) to be in line with industrial hydrogen production capacities used in the oil refinery sector. A pre-combustion CO₂ capture process based on Methyl-Diethanol-Amine (MDEA) was also considered to reduce the greenhouse gas emissions (decarbonisation of fossil LPG used). The carbon capture rate was about 78%. The evaluation was made using process flow modeling (ChemCAD) and the simulation results were compared with experimental data reported in the literature. A similar hydrogen production process from LPG reforming without carbon capture was also considered to assess the energy penalty for CO₂ capture. This work is an important study for evaluation of reducing carbon footprint in oil refinery sector.

Keywords: *Liquefied petroleum gas (LPG); Hydrogen production; Carbon capture and storage (CCS).*

INTRODUCTION

Hydrogen and liquefied petroleum gas (LPG) are one of the most often used fuels in various industrial applications. For instance, LPG is utilized in hundreds of industrial, transport and domestic applications. This fuel is composed mostly of propane, butane and ethane and it is used as a fuel for

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many residential, commercial and agricultural applications, including cooking, hot water systems and heating. LPG is also employed as a propellant, refrigerant, vehicle fuel and petrochemical feedstock [1]. Petroleum refining processes are the chemical engineering operations used in oil refineries in order to transform crude oil into useful products like liquefied petroleum gas (LPG), gasoline, diesel, kerosene, jet fuel, diesel oil and fuel oils [2].

Petroleum refineries are very developed industrial complexes that include a lot of various processing units and auxiliary facilities such as utility units and storage tanks. The primary end-products produced in petroleum refining can be grouped into four categories: light distillates, middle distillates, heavy distillates and others [3]. LPG is a light distillates product. Petroleum refinery represents one of the biggest parts of the chemical industry for the production of products from petroleum and crude oil; either by the technical method, distillation or by chemical reaction of the crude oil includes treating the raw products by a vast variety of finishing processes to yield marketable end-products. A petroleum refinery is a complex group of manufacturing plants [4].

LPG is the third most popular fuel for automotive in the world, with a number of approximate 16 million users of cars with this kind of fuel, which represent about 3% of the total market share. The countries that are shown more interest to used LPG in the transport sector are Turkey, South Korea, Poland, Italy and Australia and other countries as well, but with fewer consumers [1]. The price is the biggest motivation for using LPG in the transport sector, which is almost with 40% lower than other fuels. The second advantage is that, LPG-powered vehicles produce fewer pollutants (e.g. carbon dioxide, sulphur oxides etc.) from their exhausts in comparison with gasoline and diesel-fuelled vehicles. However, the use of this kind of fuel also has disadvantage like the installations of those cars which are become recently old and in bad condition, which can be dangerous [1]. The importance of LPG for this study is giving by the fact that it is the main raw material for the production of decarbonised hydrogen [5].

Hydrogen is the most common element in the Earth (combined as water) and also in the whole Universe with a lot of uses in very different areas. The primarily role of this chemical element is to create water which is almost the definition of life. Other industrial usage for hydrogen are in petrochemical industries, e.g. for hydrochloric acid production, methanol or ammonia production etc. It is often used as fuel because of its high calorific value and combustion generates plenty of energy [6].

The production of hydrogen can be made in several ways, for which the most common technique is hydrocarbons steam reforming. Other methods include bio-hydrogen production, thermolysis or electrolysis. Hydrogen and

steam reforming are also used by many industries. Steam reacts with methanol to generate carbon monoxide and hydrogen. The whole process is done at high temperatures. When the temperature is set down, carbon monoxide will be produced and it can produce carbon dioxide and hydrogen. The overall energy efficiency is about 65 - 75%.

Hydrogen is considered one of the cleanest fuels, because when burnt, it does not produce greenhouse gases (e.g. CO₂), only water vapor and because of that its production is very important in a lot of industries and maybe in the future would replace gasoline, oil and natural gas [7].

Hydrogen can also be obtained from the reforming of liquefied petroleum gas (LPG), which is the method that will be discussed in this article. Liquefied petroleum gas (LPG) is a mixture of hydrocarbon gases, predominantly of propane and butane. In winter, LPG contains more propane, while in summer, it contains more butane, but its average composition is about 35% propane and 65% butane [1]. LPG exists as a gas at normal atmospheric pressure and temperature, but to minimize its volume, it is liquefied at high pressure [9]. Specification of the composition of LPG is required as traces of hydrocarbon impurities which can negatively affect the fuel quality and processing [8].

According to the literature, the chemicals present in a reaction system for the steam reforming of LPG are: C₄H₁₀, C₃H₈, C₂H₆, C₂H₄, CH₄, CO, CO₂, H₂, H₂O and solid carbon (C). However, this reaction causes a side production of carbon dioxide and carbon monoxide, which are greenhouse gases and contribute to global warming [9]. The reactions which represent the system for the production of hydrogen are a set of 7 linearly independent reactions there are presented in Table 1 [10].

Table 1. Reactions of steam reforming of LPG

Reaction 1:	$C_4H_{10} + H_2O \leftrightarrow C_3H_8 + CO + 2H_2$
Reaction 2:	$C_3H_8 + H_2O \leftrightarrow C_2H_6 + CO + 2H_2$
Reaction 3:	$C_2H_6 + H_2O \leftrightarrow CH_4 + CO + 2H_2$
Reaction 4:	$C_2H_4 + H_2O \leftrightarrow CH_4 + CO + H_2$
Reaction 5:	$CH_4 + H_2O \leftrightarrow CO + 3H_2$
Reaction 6:	$CO + H_2O \leftrightarrow CO_2 + H_2$
Reaction 7:	$CO + H_2 \leftrightarrow C_{(s)} + H_2O$

The production of hydrogen from catalytic reforming of liquefied petroleum gas (LPG) is accompanied by production of carbon dioxide (CO₂) which is a greenhouse gas. The fossil CO₂ emissions need to be controlled in order to prevent or at least diminishes the global warming, melting glaciers and other environmental effects [11].

Carbon capture and storage (CCS) is the process of capturing waste carbon dioxide (CO₂) from various fossil fuels-intensive processes (e.g. power generation, metallurgy, cement, petro-chemicals etc.) [12]. Once captured CO₂ is then transport and stored to a storage site, where it will not return to the atmosphere, normally an underground geological formation. The purpose of this is to prevent the release of large quantities of carbon dioxide (CO₂) into the atmosphere, which unfortunately has the potential to induce severe climate changes.

Capturing carbon dioxide (CO₂) is most effective at emission point sources, especially in the case of chemical industries with major carbon dioxide (CO₂) emissions. Capturing CO₂ from air is also possible, but not very practical because the carbon dioxide (CO₂) is not concentrated. Impurities in this CO₂ stream, like sulphur's and water, could have a significant effect on their phase behaviour and could pose a significant threat of increased corrosion of pipeline and well materials. In instances where CO₂ impurities exist, especially with air capture, a scrubbing separation process would be needed to initially clean the flue gas and gasifying coal, it is possible to capture approximately 65% of carbon dioxide embedded in it and sequester it in a solid form [13].

The conceptual methods used for the carbon capture and storage (CCS) are the following:

- Post-combustion capture option in which the CO₂ is removed after the combustion of the fossil fuel, using for a broad range of methods e.g. gas-liquid absorption by methyl-diethanol-amine (MDEA). The post-combustion capture processes are the most popular because of existing fossil fuel power plants that can be easily retrofitted to include carbon capture and storage (CCS) technology;
- Oxy-fuel combustion option in which the fuel is burned in oxygen instead of air. This technique is promising in reducing the complexity of CO₂ separation from the flue gases (avoiding nitrogen contamination), but the initial air separation step (by cryogenic air distillation) demands a significant amount of energy and also the cost of air separation technology is significant;
- Pre-combustion CO₂ capture option which is more often applied in the fertilizer production (ammonia, urea), various chemical industries (e.g. hydrogen production) and power production. Gas-liquid absorption is the most straightforward method for pre-combustion CO₂ capture using either chemical (e.g. MEA, MDEA etc.) or physical (e.g. Selexol™, Rectisol® etc.) solvents

According to the literature, the carbon capture rate in all these three conceptual CO₂ capture processes is about 90 % to be commercially and economically viable.

PLANT CONFIGURATIONS AND MAIN DESIGN ASSUMPTIONS

Figure 1 presents the conceptual design of hydrogen production method from gas petroleum liquefied (LPG) with CCS using MDEA-based gas-liquid absorption (noted as Case 2). In this figure, the operational steps which are required in order to obtain hydrogen and in the same time also to reduce the greenhouse gas emissions, by CO₂ capture are illustrated. For CO₂ capture process, a pre-combustion configuration was used based on gas-liquid absorption process using methyl-diethanol-amine (MDEA). The hydrogen-rich gas resulted after syngas decarbonisation is purified by a Pressure Swing Adsorption (PSA) unit to the required quality specification (purity higher than 99.95 % vol.).

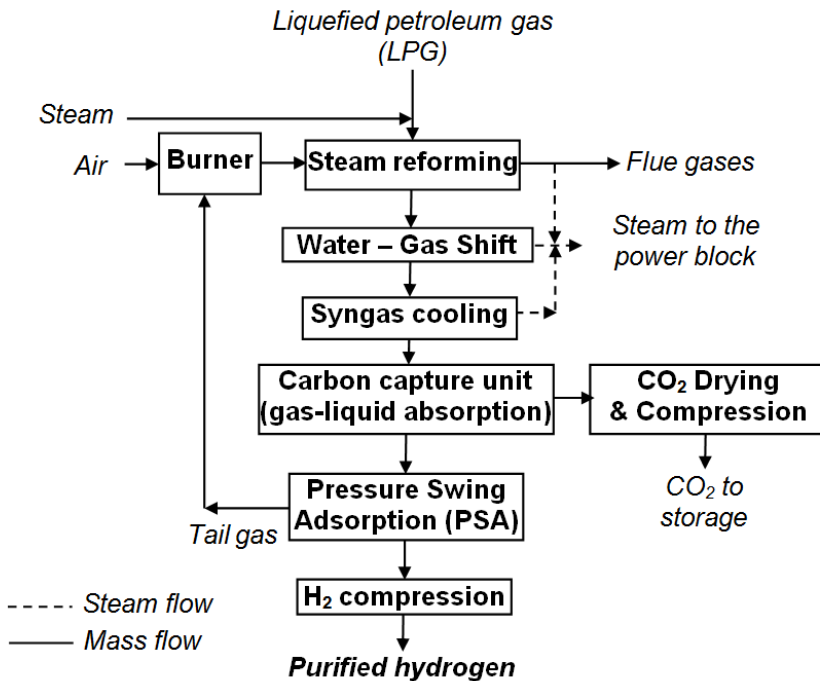


Figure 1. Hydrogen production from gas petroleum liquefied with carbon capture and storage using Methyl-Diethanol-Amine (MDEA)

Figure 2 illustrates the conceptual design of hydrogen production from gas petroleum liquefied (LPG) without carbon capture and storage (noted as Case 1). This scheme was also evaluated (as a benchmark case of

the carbon capture design) with the purpose of presented a comparison between the two hydrogen production methods by LPG catalytic reforming with and without capture and storage of carbon dioxide (CCS). This comparison has the main purpose to underline the advantages and the disadvantages of carbon capture technology. Nowadays, the implementation of CCS technologies to whole industrial sector has a remarkable importance considering the facts that the fossil fuels (oil, natural gas, coal etc.) are predicted to remain the backbone of many industrial processes as well the fact that the carbon dioxide is a greenhouse gas producing global warming.

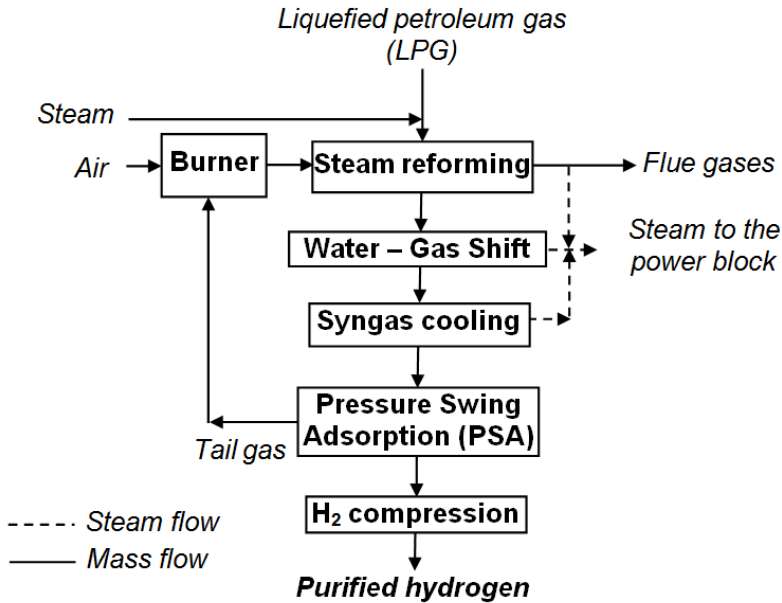


Figure 2. Hydrogen production from gas petroleum liquefied without carbon capture and storage

In order to evaluate the hydrogen production method from catalytic reforming of liquefied petroleum gas with and without carbon capture and storage, the both processes with and without CCS were assessed by a process flow modeling software (ChemCAD). Table 2 presents the main modeling assumptions used in the evaluation [14]. The developed models were validated by comparison to the literature data [11,15-16], no significant variations being noted. The simulation results were used to calculate the overall technical and environmental indicators.

Table 2. Main design assumptions of evaluated cases

Unit	Parameters
Hydrogen production capacity & purity	100000 Nm ³ /h Hydrogen purity: 99.95% (vol.)
Fuel used: liquefied petroleum gas (LPG)	Composition (% vol.): 65% butane, 35% propane Pressure: 30 bar Outlet temperature: 25°C
LPG catalytic reformer	Outlet temperature: 900°C Reactor type: Gibbs reactor Thermal mode: heat exchanger Pressure drop: 1 bar Heat duty (to be supplied by an external burner): 148 MW _{th} Overall heat of reaction: 88 MW _{th}
Water Gas Shift (WGS) conversion	Outlet temperature: 400°C Reactor type: Equilibrium reactor Thermal mode: adiabatic Steam to CO ratio: 2 (molar) Pressure drop: 1 bar
Hydrogen-rich gas (after shift conversion)	Temperature: 40°C Pressure: 28.75 bar Composition (% vol.): 73.48% hydrogen, 21.32 % carbon dioxide, 2.54 % methane, 2.38 % carbon monoxide, 0.28 % water
CO ₂ capture process	Solvent used for CO ₂ capture: methyl-diethanol-amine (MDEA) Concentration: 50 % wt.
Absorption column:	No. of stages: 30 Column pressure drop: 1 bar Top pressure: 28 bar
Desorption column:	No. of stages: 10 Column pressure drop: 1 bar Top pressure: 4 bar Reboiler duty: 18 MW _{th}
CO ₂ drying & compression	CO ₂ drying: Tri-Ethylene-Glycol (TEG) 3 compression steps with inter-cooling Final delivery pressure: 120 bar CO ₂ quality specification (vol. %) [14]: >95% CO ₂ ; <2000 ppm CO; <250 ppm H ₂ O; <100 ppm H ₂ S
Hydrogen compression unit	Delivery pressure: 60 bar Outlet temperature: 40°C
Heat recovery steam generation unit	Steam conditions: 470°C & 40 bar Steam turbine efficiency: 85 % Condensing pressure: 48 mbar
Pumps and compressors	Energy efficiency: 85 % Pressure ration: max. 3
Heat exchangers	$\Delta T_{\min.} = 10^{\circ}\text{C}$; Pressure drop: 3 - 5% of inlet pressure

RESULTS AND DISCUSSIONS

The evaluated concepts of hydrogen production from liquefied petroleum gas (LPG) catalytic reforming process with and without carbon capture were modeled and simulated using process flow modeling software (ChemCAD). The size of evaluated hydrogen production concepts was 100000 Nm³/h hydrogen with a purity of 99.95% (vol.) to be comparable with other industrial hydrogen production capacities used for instance in the oil refinery or various chemical sectors.

By comparing the two methods of obtaining hydrogen from catalytic reforming of LPG with and without capture and storage of carbon dioxide (CCS), one can evaluate the technical and environmental advantages and disadvantages of carbon capture method e.g. overall energy efficiency, energy penalty for CO₂ capture, specific CO₂ emissions etc. These technical and environmental indicators are very important in any CCS project [17].

All concepts were modeled and stimulated in a fully thermally integrated design [18]. Pinch analysis was used as main heat and power integration analysis tool with 10°C as minimum temperature difference. As an illustrative example of the thermal integration analysis, Figure 3 presents the Hot and Cold Composite Curves (HCC and CCC) for the LPG reforming case with carbon capture and storage.

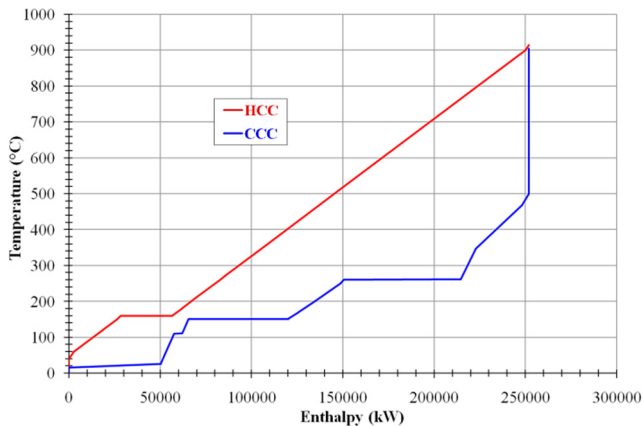


Figure 3. Hot and cold composite curves for LPG catalytic reforming with CCS

In order to assess the overall performance of the process of hydrogen production from catalytic LPG reforming, the modeling and simulation of both plant configurations yields the required process data like mass and molar flows, pressures, composition, temperatures, heat and power generated and consumed.

For the calculations of overall plant performance, the following technical and environmental indicators were used:

- **Cold gas efficiency (CGE)** represent the overall efficiency of reforming process and it is calculated with the following formula:

$$CGE = \frac{\text{Syngas thermal energy [MW}_{th}]}{\text{Feedstock thermal energy [MW}_{th}]} * 100 \quad (1)$$

- **Syngas treatment efficiency (STE)** shows the energy losses through the syngas conditioning line (shift conversion, CO₂ capture) and is calculated with the below formula:

$$STE = \frac{\text{Syngas thermal energy ex. AGR [MW}_{th}]}{\text{Syngas thermal energy ex. quench [MW}_{th}]} * 100 \quad (2)$$

- **Net electrical and hydrogen efficiencies (η_{power} and $\eta_{Hydrogen}$)** indicates conversion process. These indicators are calculated using the following formulas:

$$\eta_{power} = \frac{\text{Net power output [MW}_e]}{\text{Feedstock thermal energy [MW}_{th}]} * 100 \quad (3)$$

$$\eta_{hydrogen} = \frac{\text{Hydrogen thermal output [MW}_e]}{\text{Feedstock thermal energy [MW}_{th}]} * 100 \quad (4)$$

- **Carbon capture rate (CCR)** is obtained considering the molar flow of captured carbon dioxide divided with carbon molar flow from the feedstock (LPG):

$$CCR = \frac{\text{Captured CO}_2 \text{ molar flow [kmole/h]}}{\text{Feedstock carbon molar flow [kmole/h]}} * 100 \quad (5)$$

- **Specific CO₂ emissions (SE_{CO_2})** are calculated considering emitted CO₂ mass flow for each MW power plus hydrogen generated within the process:

$$SE_{CO_2} = \frac{\text{Emitted CO}_2 \text{ mass flow [kg/h]}}{\text{Net power + Hydrogen output [MW]}} * 100 \quad (6)$$

- **Specific Primary Energy Consumption for CO₂ Avoided (SPECCA)** is considering the energy consumption for CO₂ capture and it was calculated with the formula:

$$SPECCA = \frac{\text{Heat rate}_{\text{Capture}} \left[\frac{MJ_{LHV}}{MWh} \right] - \text{Heat rate}_{\text{No capture}} \left[\frac{MJ_{LHV}}{MWh} \right]}{\text{Emissions}_{\text{No capture}} \left[\frac{kg CO_2}{MWh} \right] - \text{Emissions}_{\text{Capture}} \left[\frac{kg CO_2}{MWh} \right]} \quad (7)$$

One of the main purposes of the modeling and simulation work for the production of hydrogen through LPG catalytic reforming was to generate the mass and energy balances to calculate the overall plant performance indicators. The technical and environmental performance indicators for the evaluated hydrogen production processes from catalytic reforming of LPG without carbon capture (Case 1) and the similar process with carbon capture (Case 2) are presented in Table 3.

Table 3. Performance indicators of hydrogen production from LPG reforming

Main Plant Data	Units	Case 1	Case 2
LPG flowrate	t/h	35.82	35.82
LPG lower heating value (LHV)	MJ/kg	45.75	
Feedstock thermal energy (A)	MW _{th}	455.27	455.27
Steam turbine output	MW _e	8.69	8.55
Expander output	MW _e	2.60	1.54
Gross power output (B)	MW _e	11.29	10.09
Hydrogen output (C)	MW _{th}	300.00	300.00
CO ₂ capture & compression	MW _e	0.00	5.71
Hydrogen compression	MW _e	3.89	3.88
Power island	MW _e	0.18	0.19
Ancillary consumption (D)	MW _e	4.07	9.78
Net power output (E = B - D)	MW _e	7.22	0.31
Net power efficiency (E/A * 100)	%	1.58	0.06
Hydrogen efficiency (C/A * 100)	%	65.89	65.89
Cumulative energy efficiency	%	67.47	65.95
Carbon capture rate	%	0.00	78.87
CO ₂ specific emissions (H ₂ +power)	kg/MWh	351.77	75.97
SPECCA	MJ/kg CO ₂	-	0.44

As can be noticed from Table 3, the hydrogen production process without CCS (Case 1) is slightly more efficient than the concept with CCS (Case 2) by about 1.5 net energy (hydrogen + power) efficiency percentage points. Comparing this energy penalty for CO₂ capture with literature data [17,19] for other energy conversion systems with CCS (e.g. natural gas catalytic reforming, coal gasification etc.) one can notice that the LPG catalytic reforming

process is combining a high energy efficiency with low energy penalty for CO₂ capture. The carbon capture rate of Case 2 is about 79 % in line with other pre-combustion CO₂ capture concepts applied for hydrocarbon reforming processes (e.g. natural gas, naphtha etc.) [20-21]. The specific primary energy consumption for CO₂ avoided (SPECCA) is also promising in comparison to other CO₂ capture methods (e.g. post-combustion capture option has a SPECCA value of about 3 MJ/kg CO₂).

CONCLUSIONS

This paper evaluates the technical and environmental performances of hydrogen production (as a clean decarbonised fuel) from catalytic reforming of liquefied petroleum gas (LPG) with and without carbon capture and storage (CCS). A hydrogen production unit with 100000 Nm³/h (corresponding to 300 MW thermal output) was evaluated. The simulation results showed that the carbon capture concept (Case 2) has an overall energy efficiency with just about 1.5 net efficiency percentage points (as CO₂ capture energy penalty) lower compared to the case without carbon capture (Case 1). The carbon capture rate for Case 2 was about 79 % and the specific CO₂ emissions per MW of produced energy (hydrogen and power) are decreasing accordingly. The specific primary energy consumption for CO₂ avoided (SPECCA) is also very promising for the hydrogen production through LPG reforming with CCS.

In conclusion, the proposed LPG catalytic reforming process with carbon capture is a very promising option for reducing the CO₂ emissions from hydrogen production processes (as the case of oil refinery sector as well as other large scale chemical applications e.g. ammonia, fertilizers).

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REFERENCES

1. D. Brzezinska, A.S. Markowski, *Process Safety and Environmental Protection*, **2016**, 116, 90.
2. E. Elnajjar, M.O. Hamdan, M.Y.E. Selim, *Renewable Energy*, **2013**, 56, 110.
3. R.F. Colwell, *Excellence in Applied Chemical Engineering*, **2009**.
4. D. James, H. Gary, G.E. Handwerk, M.J. Kaiser, "Petroleum Refining: Technology and Economics", Fifth Edition, **2007**.
5. C.Y. Li, J.Y. Wu, C.Y. Zheng, R.Z. Wang, *Applied Thermal Engineering*, **2017**, 115, 315.
6. J. Kim, C. Bae, G. Kim, *Fuel*, **2016**, 183, 304.
7. A. Boretti, *Fuel Processing Technology*, **2017**, 161, 41.
8. A. Ruissen, "The Analysis of Hydrocarbon Composition in LPG by Gas Chromatography using the DVLS Liquefied Gas Injector", PhD Thesis, *Da Vinci Laboratory Solutions B.V.*
9. Technical Data for Propane, Butane, and LPG Mixtures, Alternate Energy Systems, Inc.
10. J.A. Sousa, P.P. Silva, A.E.H. Machado, M.H.M. Reis, L.L. Romanielo, C.E. Hori, *Brazilian Journal of Chemical Engineering*, **2013**, 30, 83.
11. International Energy Agency - *Greenhouse gas R & D Programme* "Decarbonisation of fossil fuels", March **1996**.
12. G. Lozza, P. Chiesa, "Natural gas decarbonization to reduce CO₂ emission from combined cycles, Part B: Steam-methane reforming", *Proceedings of ASME TURBOEXPO* May 8-11, Munich Germany, **2000**.
13. E. Elnajjar, M.Y.E. Selim, M.O. Hamdan, *Energy Conversion and Management*, **2013**, 76, 32.
14. C.C. Cormos, K. Vatopoulos, E. Tzimas, *Energy*, **2013**, 51, 37.
15. M. Voldsund, K. Jordal, R. Anantharaman, *International Journal of Hydrogen Energy*, **2016**, 41, 4969.
16. P. Nikolaidis, A. Poullikkas, *Renewable and Sustainable Energy Reviews*, **2017**, 67, 597.
17. B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer, Carbon Dioxide Capture and Storage, Intergovernmental Panel on Climate Change (IPCC), Geneva, Switzerland, **2005**.
18. C.C. Cormos, *International Journal of Hydrogen Energy*, **2010**, 35, 7485.
19. O. de Queiroz F. Araújo, J.L. de Medeiros, *Current Opinion in Chemical Engineering*, **2017**, 17, 22.
20. N. Muradov, *International Journal of Hydrogen Energy*, **2017**, 42, 14058.
21. International Energy Agency - *Greenhouse gas R & D Programme* "The reduction of greenhouse gas emissions from the oil refinery and petrochemical industry", June **1999**.