NAFTA-GAZ

Nafta-Gaz 2024, no. 12, pp. 767–778, DOI: 10.18668/NG.2024.12.06

Simulation of direct dimethyl ether (DME) synthesis using existing methanol production infrastructure in Arzew, Algeria

Symulacja bezpośredniej syntezy eteru dimetylowego (DME) z wykorzystaniem istniejącej infrastruktury produkcji metanolu w Arziwie, Algieria

Ilhem Sidi-Yacoub, Ahmed Feddag, Ikram Khelifa

Abdelhamid Ibn Badis University, Algeria

ABSTRACT: This study investigates the direct synthesis of dimethyl ether (DME) from syngas using the existing methanol production infrastructure at the Methanol and Synthetic Resins complex in Arzew, Algeria. The primary objective is to assess the feasibility of repurposing the adiabatic multiphase fixed-bed methanol production reactor for DME production while maintaining the original reactor dimensions, flow conditions, syngas composition, as well as temperature and pressure parameters used in methanol production. The research introduced a significant modification by replacing the initial copper oxide-based catalyst with a hybrid catalyst composed of γ-alumina and $CuO/ZnO/Al_2O_3$. This catalyst enables the direct production of DME from syngas, which is a mixture of carbon dioxide, carbon monoxide, and hydrogen. The study employed simulation models using Aspen-HYSYS V11 to predict DME productivity, manage the high temperatures resulting from exothermic reactions in each catalyst bed, and determine the required quench gas injection for temperature reduction. The simulation results indicated an overall DME yield of 2.81%, which is comparable to the methanol production rate of 3%. Further simulations with recycling stages increased the crude DME mass to 4.11%. These findings highlight the potential of using the current infrastructure to improve profitability and time efficiency in producing this alternative fuel.

Key words: dimethyl ether (DME); simulation; synthesis gas; Aspen-HYSYS; Arzew methanol reactor.

STRESZCZENIE: W ramach niniejszej pracy przeanalizowano możliwość bezpośredniej syntezy eteru dimetylowego (DME) z gazu syntezowego z wykorzystaniem istniejącej infrastruktury produkcji metanolu w kompleksie Methanol and Synthetic Resins w Arziwie w Algierii. Głównym celem jest ocena możliwości adaptacji adiabatycznego wielofazowego reaktora produkcji metanolu ze złożem stałym do produkcji DME przy zachowaniu oryginalnych wymiarów reaktora, warunków przepływu, składu gazu syntezowego, a także parametrów temperatury i ciśnienia stosowanych w produkcji metanolu. W badaniach wprowadzono znaczącą modyfikację poprzez zastąpienie początkowego katalizatora na bazie tlenku miedzi katalizatorem hybrydowym składającym się z γ-tlenku glinu i $CuO/ZnO/Al_2O_3$. Katalizator ten umożliwia bezpośrednią produkcję DME z gazu syntezowego, który jest mieszaniną dwutlenku węgla, tlenku węgla i wodoru. W badaniu zastosowano modele symulacyjne wykorzystujące Aspen-HYSYS V11, co pozwoliło przewidzieć wydajność DME, kontrolować wysokie temperatury wynikające z reakcji egzotermicznych w każdym złożu katalizatora oraz określić ilość gazu chłodzącego potrzebnego do redukcji temperatury. Wyniki symulacji wykazały ogólną wydajność DME na poziomie 2,81%, co jest porównywalne ze wskaźnikiem produkcji metanolu wynoszącym 3%. Dalsze symulacje z zastosowaniem etapów recyklingu zwiększyły masę surowego DME do 4,11%. Wyniki te podkreślają potencjał wykorzystania obecnej infrastruktury do poprawy rentowności i efektywności czasowej w produkcji tego alternatywnego paliwa.

Słowa kluczowe: eter dimetylowy (DME); symulacja; gaz syntezowy; Aspen-HYSYS; reaktor metanolowy w Arziwie.

Introduction

Algeria produces methanol through the Methanol and Derivatives Complex (CP1Z) located at the Arzew refinery in the industrial zone approximately 40 kilometers from Oran on the western coast of Algeria. This complex has an annual production capacity of about 113,000 tons of methanol, with at least 92% of its production allocated for export (MINES, 2024). Importing countries convert methanol into hydrocarbons using the Methanol-to-Gasoline (MTG) process developed by Mobil, enabling the selective production of high-octane gasoline (Guisnet and Ramôa, 2006).

Corresponding author: S.-Y. Ilhem, e-mail: *Ilhem.s.y@gmail.com*

Article contributed to the Editor: 25.07.2024. Approved for publication: 11.12.2024.

The MTG technology is an advanced chemical process that converts raw methanol into dimethyl ether (DME) using acidic catalysts. Subsequently, this mixture passes through a reactor containing an H-ZSM-5 catalyst, converting it into a hydrocarbon blend with high selectivity for gasoline (Yurchak, 1988), as illustrated in the following diagram.

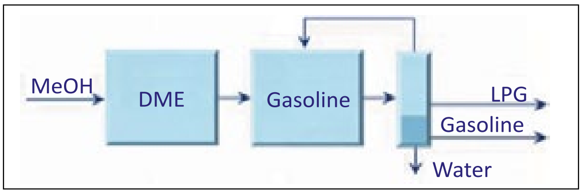

Figure 1. Methanol-to-gasoline (MTG) process (Olsbye et al., 2012)

Rysunek 1. Proces przetwarzania metanolu w benzynę (MTG) (Olsbye et al., 2012)

The aim of this study is to assess the feasibility of repurposing existing industrial infrastructure designed for methanol synthesis for dimethyl ether (DME) production. Simulations were conducted for the direct synthesis of DME using the methanol reactor located in the CP1Z complex in Arzew, maintaining the original reactor dimensions, synthetic gas composition, and operating conditions, including temperature and pressure. The only modification made was the catalyst, where a hybrid catalyst consisting of a mixture of copper oxide and acidic catalysts was used.

This research advocates for the direct production of DME in Algeria instead of exporting methanol, potentially reducing costs for both exporting and importing countries due to the similarities in methanol and DME synthesis processes. For methanol-producing nations, DME production presents a more profitable and efficient alternative. DME serves as a clean fuel option with significant environmental advantages, driving its demand in regions with stringent environmental regulations. Its capacity to substitute diesel and liquefied petroleum gas has spurred interest and applications across various industries (Arcoumanis et al., 2008).

The escalating demand for clean fuels positions DME as a strategic choice, supported by its increasing price over time owing to sustainability and effectiveness in reducing harmful emissions (Jaiyeola et al., 2022). DME production enhances the economies of methanol-producing countries, opening new opportunities in the clean fuel market and bolstering their competitive edge (Fleisch et al., 2012). For importing nations, utilizing imported DME streamlines and enhances the methanol--to-gasoline (MTG) process, facilitating the direct conversion of DME into gasoline and subsequent transformation into liquefied petroleum gas (LPG). Moreover, DME acts as an efficient aerosol propellant, featuring rapid decomposition into carbon dioxide (CO_2) and water within one day (Ramadhas, 2011), confirming its environmental superiority. Recent developments position DME as a very promising alternative fuel for diesel engines, meeting stringent performance standards. Since its inception as an attractive alternative to diesel fuel in the 1950s, interest in DME has increased due to its beneficial properties, including nearly smokeless combustion facilitated by a low auto-ignition temperature, rapid evaporation upon cylinder injection, and high oxygen content (about 35% by mass), and the absence of C-C bonds in its molecular structure, all of which contribute to cleaner and more efficient combustion processes (Ju et al., 2009).

This study was conducted using Aspen HYSYS V11, a leading software for modeling, simulation, and optimization of industrial processes, widely utilized in the petrochemical sector (Alnili and Barifcani, 2018; Procédés..., 2024). This software is well-known for its excellence in process design, control, and enhancement. It provides a comprehensive range of unit operations and accurately characterizes the properties of solid catalysts as well as the kinetics of heterogeneous chemical reactions (Adeniyi et al., 2018). By integrating thermodynamic, kinetic, and hydrodynamic aspects, Aspen HYSYS enables highly precise simulation of complex system behaviors.

Dimethyl ether synthesis

Synthesis of dimethyl ether (DME) from synthesis gas ($CO/CO_2/H_2$) is currently a topic of significant interest. Two main synthesis methods have been developed: indirect and direct synthesis.as illustrated in the following figure.

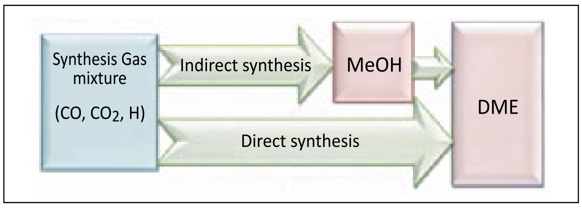

Figure 2. Diagram of DME production

Rysunek 2. Schemat produkcji DME

Indirect synthesis of DME involves a two-step process. Initially, methanol is synthesized from $CO_2/CO/H_2$ in a high-pressure reactor operating between 50 and 100 bar at moderate temperatures of 220–280°C, utilizing a $CuO/ZnO/Al_2O_3$ catalyst (Ramadhas, 2011). Subsequently, the methanol is dehydrated and converted to DME in a second reactor using solid acid catalysts such as γ-Al_2O_3 or HZSM-5 zeolite, with operational temperatures ranging from 100 to 300°C and pressures up to

50 bar (Maji et al., 2015). In contrast, direct synthesis converts syngas to DME in a single step within a single reactor using hybrid catalysts that integrate $Cu/ZnO/Al_2O_3$ for methanol synthesis and solid acids for methanol dehydration. This process typically operates at temperatures of 200–300°C and pressures of 50–100 bar (Giuliano et al., 2021).

In this study, we chose to model the direct method for dimethyl ether synthesis due to its single-step reaction advantage, which streamlines the process and could potentially lower costs. Furthermore, the use of synthesis gas from renewable sources supports sustainability efforts in DME production.

Process pverview

The synthesis is conducted using the ICI (Imperial Chemical Industries) process in an adiabatic fixed-bed reactor designed as a vertical cylindrical vessel (Bendjaouahdou and Bendjaouahdou, 2014). This reactor comprises four catalyst beds arranged in series, each bed containing densely packed catalyst particles. Each bed is filled with compact and stationary catalyst particles, as depicted in Figure 3.

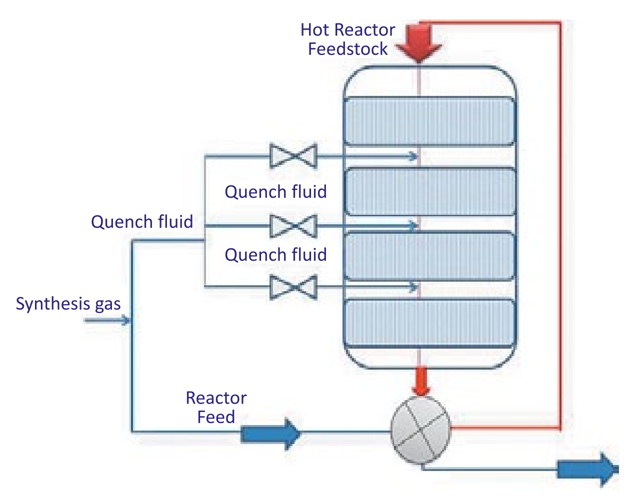

Figure 3. Multi-bed reactor with quenching systems

Rysunek 3. Reaktor wielowarstwowy z systemem chłodzenia

Operating temperatures range from approximately 210°C to 270°C, while the pressure is consistently maintained at 52 bars (Ortiz et al., 2013). Given the exothermic nature of the reaction, effective heat management is crucial to maintain optimal operational conditions. To regulate temperature and dissipate excess heat, cold synthesis gas, known as quench gas, is introduced between the catalyst layers (Lee, 1989). This quench gas cools the reaction mixture, thereby regulating and maintaining the desired temperature levels within the reactor.

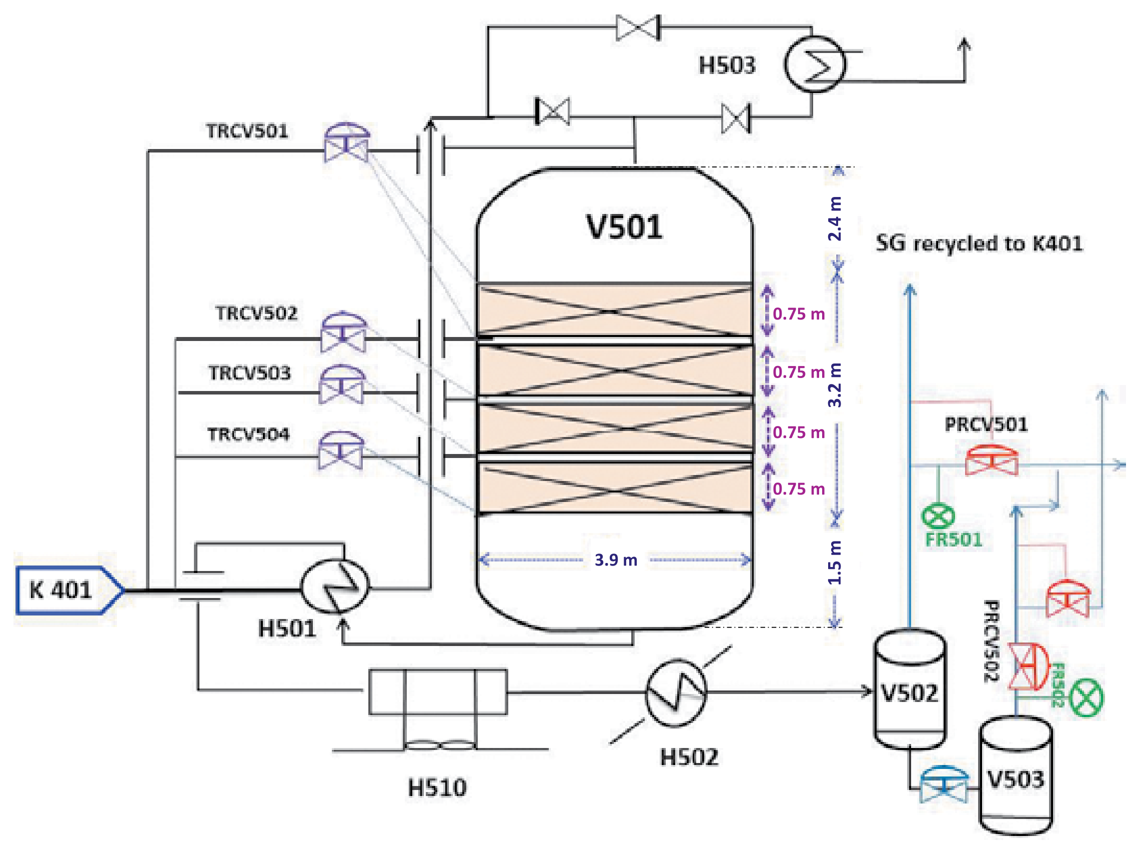

Figure 4. Catalytic reactor of the CP1Z complex in Arzew

Rysunek 4. Reaktor katalityczny kompleksu CP1Z w Arziwie

Precise temperature control maximizes reaction efficiency and ensures continuous operation.

As shown in the Figure 4, the initial step involves mixing synthesis gas with recycled gas. The resulting mixture is then compressed and split into two streams: the first stream undergoes preheating via thermal exchange with reactor effluent before entering the reactor, while the second stream serves as the cold quenching fluid. The effluent exiting the reactor is cooled and separated to recover crude DME. Unreacted gas is recycled, with a small portion purged to prevent inert compound accumulation in the reaction loop.

Tables 1 and 2 exhibit the technical data concerning the Arzew reactor that we respected in this simulation.

Table 1. Operating conditions of the reactor

Tabela 1. Warunki pracy reaktora

Parameters	Value
Reactor inlet flow rate [kmol/h]	14220
First catalytic bed flow rate [kmol/h]	9960
Quench gas flow rate [kmol/h]	4260
Inlet pressure [bar]	52
Inlet temperature [°C]	230
Quench gas temperature [°C]	70

Table 2. Characteristics of the reactor

Tabela 2. Specyfikacja reaktora

Parameters	Value
Number of catalytic beds	4
Height of each catalytic beds [m]	0.75
Reactor diameter [m]	3.9

Table 3 delineates the gas mixture composition at the inlet of the Arzew reactor.

Table 3. Molar composition of the synthesis gas

Tabela 3. Skład molowy gazu syntezowego

Feed composition	Molar fraction [%]
CO	7.50
CO_2	6.00
H_2	73.70
H_2O	0.13
N_2	3.26
CH_4	9.36

Modeling the Arzew reactor for DME synthesis

The synthesis of dimethyl ether (DME) is a heterogeneous process characterized by rapid reactions and significant thermal effects. Due to the inherent complexity of heterogeneous catalytic reactors, several assumptions were made to simplify the calculations and modeling of this system. These assumptions are as follows:

We adopted the one-dimensional pseudo-homogeneous model, commonly referred to as the piston flow model (PFR) (Elnashaie, 1994), to simplify the modeling of the Arzew reactor for DME synthesis, based on previous studies in the field (Froment, 1972). This model assumes phase homogeneity, where the catalytic surface is uniformly exposed to gas-phase conditions, ensuring uniformity of variables such as temperature, concentration, and pressure across the catalyst surface. Additionally, the model considers the fluid and catalyst as a single phase with constant fluid properties throughout the reactor length. These simplifications reduce mathematical complexity in reactor modeling while maintaining sufficient predictive accuracy.

Therefore, we proceeded to model the Arzew Multi-bed Adiabatic Reactor Using PFR-HYSYS, along with the following considerations:

- Simplicity and implementation: According to Froment's (Froment, 1972) classification of fixed-bed reactor models, the one-dimensional piston flow reactor (PFR) model is the simplest among pseudo-homogeneous models. Its simplicity makes it easier to implement and interpret compared to more complex models that account for additional factors and interactions.
- Common use in cylindrical geometries: The PFR model is widely employed to describe chemical reactions in continuous systems with cylindrical geometry, allowing for prediction of various chemical reactors behavior (Wijayarathne and Wasalathilake, 2014; Kumar, 2015; Ramos et al., 2022).
- Incorporation of heterogeneous catalytic reactions: The PFR-HYSYS model allows the incorporation of heterogeneous catalytic reactions using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) methodology. ASPEN-HYSYS employs this integral equation, derived from the kinetics and parameters established by Bussche and Froment (1996), to accurately describe the kinetics of DME production (Tripodi et al., 2017). The LHHW kinetic model consists of three key components: a kinetic factor, a driving force expression, and an adsorption term (Al-Malah, 2022).

$$r = \left(\text{kinetic\_factor}\right)\frac{\left(\text{driving\_force}\right)}{\left(\text{adsorption\_term}\right)} \tag{1}$$

where: r – is the rate of reaction [kgmol/m^3-sec].

- Adiabatic conditions: The PFR-HYSYS model includes an optional energy stream for heat storage or dissipation. When the duty (heat transferred) is set to zero, Hysys assumes the system operates adiabatically (Hysys, 2004), meaning no heat exchange with the surroundings. This feature aligns perfectly with the conditions of the adiabatic fixed-bed reactor at Arzew.

- Simplified sub-volume representation: The PFR-HYSYS model represents a tubular reactor divided into sub-volumes, initially set at 20 by default (Hysys, 2004) However, in our study, we simplified this by reducing the number to a single sub-volume to more accurately represent the cylindrical vessel of the reactor in our simulation mode (Sidi-Yacoub et al., 2023).

Technical challenges in modeling multi-stage reactors

The multi-stage reactor at Arzew comprises four catalytic beds, with cold synthesis gas (quench gas) injected between these beds. This injection helps dissipate excess heat generated by exothermic reactions, ensuring the temperature remains within optimal limits to sustain reaction efficiency and prevent catalyst deactivation.

During our simulation, we encountered a challenge due to the absence of a pre-existing model for multi-stage reactors in the Aspen HYSYS library. To address this limitation, we represented each catalytic bed using a PFR-HYSYS reactor with a diameter equal to that of the original methanol production reactor and a height equal to the height of each catalytic layer (Sidi-Yacoub et al., 2023), as illustrated in Figure 5. This approach allowed us to simulate the behavior of the catalytic beds and the injection of quench gas between them.

Using these approaches, we developed a robust and accurate model to predict the behavior of the DME synthesis reactor under various operating conditions, while optimizing the operating parameters to improve the overall efficiency of the process.

Bifunctional catalysis for dimethyl ether synthesis

In this study, we utilized a bifunctional catalyst for the direct synthesis of dimethyl ether (DME). This catalyst comprises two main components: a metal oxide for methanol synthesis and an acidic function for dehydrating methanol to DME. The acidic function is provided by solid acids, with zeolites and γ-alumina being the most common due to their optimal acid strength and high efficiency. For this research, γ-alumina was chosen for its superior efficiency, cost-effectiveness, and thermal and mechanical resistance.

The catalysts were arranged in two layers within the catalyst basket. The upper layer consists of $CuO/ZnO/Al_2O_3$ (copper oxide/zinc oxide/aluminum oxide), while the lower layer is made of γ-alumina. Typically, the ratio of methanol-forming catalysts to dehydration catalysts is 2:1 (Ng et al., 1999). This configuration enhances the overall efficiency of the chemical reaction, with the upper catalyst facilitating methanol formation and the lower catalyst carrying out the dehydration process to produce DME. The following table outlines the properties of the catalyst used in this study.

Table 4. Catalyst properties

Tabela 4. Właściwości katalizatora

Parameters	Value
Solid Density	1783.8 kg/m^3-solide
Particle Diameter	6 mm
Particle Void Fraction	0.38

Kinetic theory of reactions

The synthesis of dimethyl ether (DME) from synthesis gas, predominantly composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and water vapor (H_2O), involves three primary catalytic reactions:

1. Methanol synthesis reaction:
   $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ $\Delta H_0 = –49.43$ kJ/mol
   (Equation 1)
2. Water gas shift (WGS) reaction:
   $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H_0 = –41.20$ kJ/mol
   (Equation 2)
3. Methanol dehydration to DME:
   $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ $\Delta H_0 = –23.40$ kJ/mol
   (Equation 3)

- Equation (1) describes the synthesis of methanol through the hydrogenation of carbon dioxide.
- Equation (2) represents the water gas shift reaction, which converts carbon monoxide (CO) and water vapor (H_2O) into carbon dioxide (CO_2) and hydrogen (H_2). Both reactions are catalyzed by the methanol synthesis catalyst ($CuO/ZnO/Al_2O_3$).
- Equation (3) denotes the methanol dehydration reaction to dimethyl ether (DME), catalyzed by an acidic catalyst (γ-alumina) (Hadipour and Sohrabi, 2008).

These reactions collectively elucidate the process of DME production from synthesis gas. The kinetic model is derived from the kinetic equations formulated by Bussche and Bercic (Bercic and Levec, 1992; Bussche and Froment, 1996).

The kinetic equations are presented as follows:

$$r_{\mathrm{CO_2\ hydrogenation}} = \frac{K_1(P_{\mathrm{H_2}}P_{\mathrm{CO_2}})[1-(1-K_{equ1})(P_{\mathrm{CH_3OH}}P_{\mathrm{H_2O}})/(P_{\mathrm{CO_2}}{P_{\mathrm{H_2}}}^3)]}{\left[1+K_2(P_{\mathrm{H_2O}}/P_{\mathrm{H_2}})+\sqrt{K_3P_{\mathrm{H_2}}}+K_4P_{\mathrm{H_2O}}\right]^3} \quad (2)$$

$$r_{\mathrm{WGSR}} = \frac{K_5P_{\mathrm{CO_2}}\left[1-K_{equ2}(P_{\mathrm{CO_2}}P_{\mathrm{H_2O}})/(P_{\mathrm{CO_2}}P_{\mathrm{H_2}})\right]}{1+K_2(P_{\mathrm{H_2O}}/P_{\mathrm{H_2}})+\sqrt{K_3P_{\mathrm{H_2}}}+K_4P_{\mathrm{H_2O}}} \quad (3)$$

$$r_{\mathrm{DME}} = K_6 K^2_{\mathrm{CH_3OH}} \left[\frac{C^2_{\mathrm{CH_3OH}} - (C_{\mathrm{H_2O}} C_{\mathrm{DME}} / K_{equ3})}{\left(1 + 2\sqrt{K_{\mathrm{CH_3OH}} C_{\mathrm{CH_3OH}}} + K_{\mathrm{H_2O}} C_{\mathrm{H_2O}}\right)^4} \right] \quad (4)$$

where:

P_i – partial pressure of component i [bar],

C_i – concentration of component i [kgmol/m^3],

K_i – adsorption equilibrium constant for component i [m^3/kgmol-sec],

K_{equ} – equilibrium constants.

The equilibrium constants for each reaction are sourced from the following literature (Stull et al., 1969; Twigg, 2018).

Table 5. Kinetic constants of reactions 1, 2, and 3

Tabela 5. Stałe kinetyczne reakcji 1, 2 i 3

$K = A \exp (B/RT)$	A	B
K_1	1.65	36 696
K_2	3610	0
K_3	0.37	17 197
K_4	7.14×10^{-11}	124 119
K_5	1.09×10^{10}	−94 765
K_{CH3OH}	0.00079	70 500
K_6	3.7×10^{10}	−105 000
K_{H2O}	0.084	41 100

where:

A – frequency factor,

B – activation energy [kJ/mol],

R – universal gas constant [8.314 J/(mol·K)],

T – temperature [K°].

The values of the kinetic parameters in the kinetic expressions are summarized above (Stull et al., 1969):

$$\log_{10} K_{equ1} = \frac{3066}{T} - 10.592 \quad (5)$$

$$\log_{10} \frac{1}{K_{equ2}} = -\frac{2073}{T} + 2.029 \quad (6)$$

$$\log_{10} K_{equ3} = \frac{10194}{T} - 13.91 \quad (7)$$

Fluid package

For the simulation of the dimethyl ether (DME) synthesis process, we utilized the PRSV (Peng-Robinson-Stryjek-Vera) thermodynamic model. This modified version of the Peng-Robinson equation of state is known for its accuracy in calculating the equilibrium of non-ideal systems, particularly those involved in the methanol dehydration reaction to produce DME. The PRSV equation is specifically effective for polar compounds, improving the representation of vapor pressure for both pure components and mixtures (van der Stelt et al., 2012).

The PRSV model has been successfully applied to vapor-liquid equilibrium calculations over a wide range of temperatures, including low reduced temperatures (Stryjek and Vera, 1986). Its capabilities make it an ideal choice for modeling and optimizing DME production, ensuring accurate evaluation of operating conditions and reactor performance.

The thermodynamic properties calculated by the PRSV model are determined by the following relationships (Rodio et al., 2021):

$$p = \frac{RT}{v-b}\frac{a}{v^2 2bv - b^2} \quad (8)$$

$$a = (0.457235 R^2 T_c^{\,2} / p_c) \cdot \alpha(T) \quad (9)$$

$$b = 0.077796 RT_c / p_c \quad (10)$$

$$\alpha(T_r) = \left[1 + K(1 - T_r^{0,5})\right]^2 \quad (11)$$

$$K = 0.378893 + 1.4897153\omega - \\ -0.1713184\omega^2 + 0.0196554\omega^3 \quad (12)$$

$$T_r = \frac{T}{T_c} \quad (13)$$

The terms are defined as follows:

a – accounts for intermolecular forces [(atm (L^3)^2)/(mol)^2],

b – adjusts for molecular size [L/mol],

K – correlation factor (dimensionless),

P_c – the critical pressure [bar],

T – temperature [C°],

T_c – the critical temperature [C°],

T_r – reduced temperature (dimensionless),

v – the molar volume [m^3/k mol],

α – dimensionless function of reduced temperature and acentric factor,

ω – the acentric factor (dimensionless).

Process simulation

The synthesis gas, initially at 50 bars and 70°C, is compressed to 52 bars and then split into two streams. One stream is preheated to 230°C in a tubular heat exchanger using heat from the reactor effluent, serving as the reactor feed. The second stream, initially at 70°C, acts as a quench gas to cool the reactants. The gaseous reaction mixture flows through four catalytic stages (modeled as small PFRs in Aspen HYSYS), from top to bottom, as shown in Figure 5.

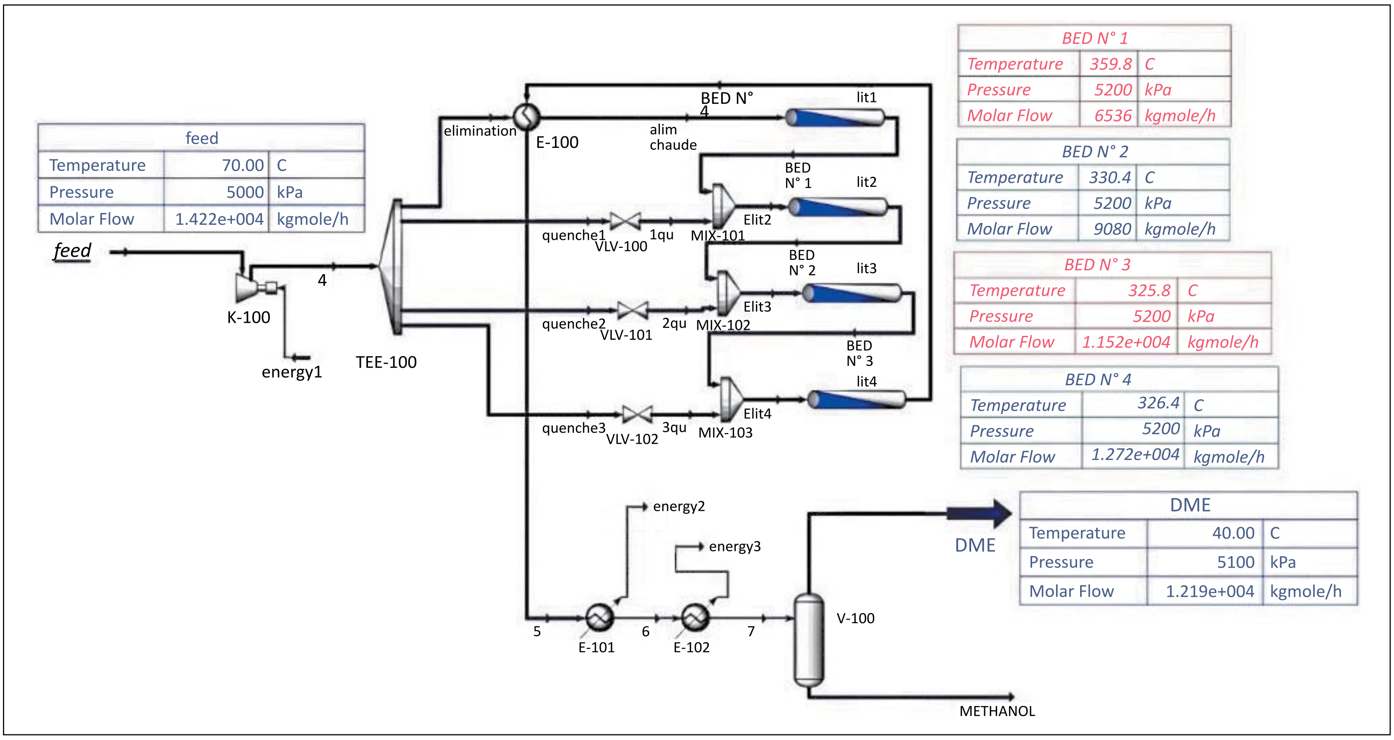

Figure 5. Flowsheet of the DME process designed in Aspen HYSYS

Rysunek 5. Schemat przepływu procesu DME zaprojektowany w Aspen HYSYS

Cold synthesis gas is introduced between catalyst layers. Each bed's effluent is mixed with quench gas to maintain temperatures between 230°C and 330°C.

The reactor effluent is cooled successively: first to 270°C in a tubular heat exchanger, then to 60°C using air-cooled heat exchangers, and finally to 40°C with water-cooled heat exchangers. A flash separator then separates and recovers crude dimethyl ether from methanol.

Results analysis

The results of the dimethyl ether (DME) production reactor simulation, detailing the molar fraction ratios of reactants and products at each of the four catalytic bed levels, are summarized in Table 6.

The simulation results presented in Table 6 indicate a gradual increase in the molar fraction of dimethyl ether (DME) from 2.09% in the first catalyst bed to 2.81% in the fourth catalyst bed. This progressive increase demonstrates the effectiveness of the methanol dehydration reaction to form DME, as the reaction continues efficiently as the synthesis gas passes through the catalytic beds. The final achieved ratio of DME in the fourth catalyst bed, at 2.81%, is significant compared to the theoretical production ratio of methanol, which is approximately 3% due to thermodynamic constraints.

Additionally, the proportions of CO and CO_2 decrease gradually from the first to the fourth catalyst bed due to the water-gas shift reaction, which converts CO to CO_2. Subsequently, CO_2 is further converted to methanol by the reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \leftrightarrow CH_3OH + H_2O \qquad (14)$$

Table 6. Molar fraction of the reaction mixture at the outlet of each catalytic bed

Tabela 6. Frakcja molowa mieszaniny reakcyjnej na wylocie każdego złoża katalitycznego

Composition [molar fraction %]	Synthesis gas	First catalyst bed	Second catalyst bed	Third catalyst bed	Fourth catalyst bed
CO	7.5	5.38	4.54	3.09	3.66
CO_2	6.0	4.94	5.41	5.50	5.48
H_2	73.7	69.91	70.07	69.67	69.42
H_2O	0	3.69	3.41	3.80	4.06
MeOH	**0**	**0.22**	**0.44**	**0.43**	**0.39**
DME	**0**	**2.09**	**2.23**	**2.61**	**2.81**

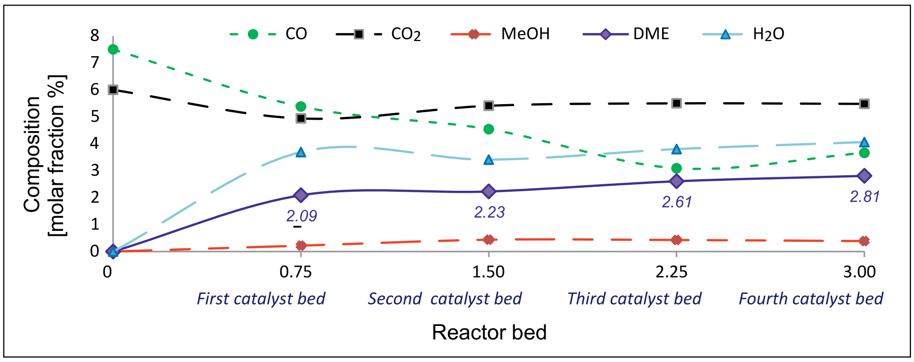

Figure 6. Concentration profiles of components at the outlet of each catalytic bed
Rysunek 6. Profile stężenia składników na wylocie każdego złoża katalitycznego

Numerous studies support this assertion (Nestler et al., 2018), indicating that methanol synthesis predominantly occurs via the hydrogenation of carbon dioxide rather than carbon monoxide. Therefore, it is crucial to consider the water-gas shift reaction when describing the methanol and dimethyl ether synthesis processes.

Figure 6 illustrates the concentration profiles of the main components inside the chemical reactor.

It is observed that methanol concentrations remain relatively low and stable across the four catalytic layers, which is attributed to its rapid conversion to dimethyl ether (DME) upon formation. This underscores the effectiveness of the hybrid catalyst containing γ-alumina, which is responsible for the dehydration of methanol and its conversion into DME. It has been demonstrated to be well suited for the conditions simulated in this study.

The findings underscore that the use of methanol reactor can be effective not only in methanol production, but also for dimethyl ether synthesis. The ability to convert methanol directly to dimethyl ether using the hybrid catalyst increases the efficiency of the synthesis process and opens new avenues for using traditional methanol reactors in the production of value-added chemical compounds.

Recycling of unconverted gas

Upon analyzing the results of the simulation operations, it is evident that dimethyl ether (DME) production is limited to approximately 2.9% due to dynamic thermal constraints. Although this rate is comparable to the 3% methanol production rate, it indicates a low conversion rate in both processes.

With a significant amount of unconverted reactants in the gas stream exiting the reactor, recovery of this unconverted synthesis gas and unreacted methanol is essential for reintroduction into the synthesis loop. This step is aimed at increasing the DME synthesis rate. Table 7 shows the production rates of dimethyl ether and other components obtained following the gas recycling simulation.

The simulation results showed significant improvements in dimethyl ether (DME) production rates across the four catalytic beds, with a production rate of 4.14% as illustrated in Figure 7.

This increase represents a significant improvement over initial results and demonstrates the effectiveness of the recycling process in increasing DME production rates. The recovery and reintroduction of these components into the synthesis loop are crucial steps towards improving the overall process efficiency.

The results confirm the feasibility of directly synthesizing DME using the existing methanol production infrastructure in Arzew by modifying the catalysts to employ a combination of gamma-alumina and $CuO/ZnO/Al_2O_3$ for DME synthesis. The original reactor dimensions and operating conditions were maintained to ensure process effectiveness.

The next step involved studying temperature variations during the DME synthesis simulation to verify the effectiveness of using the same basic operating conditions.

Table 7. Molar fractions of reaction components in each catalytic bed following recirculation
Tabela 7. Frakcje molowe składników reakcji w każdym złożu katalitycznym po recyrkulacji

Composition [molar fraction %]	First catalyst bed	Second catalyst bed	Third catalyst bed	Fourth catalyst bed
CO	9.69	9.09	8.59	8.26
CO_2	9.01	9.24	9.41	9.55
H_2	67.41	67.16	66.94	66.76
H_2O	3.81	4.02	4.20	4.36
MeOH	**0.33**	**0.33**	**0.33**	**0.33**
DME	**3.30**	**3.66**	**3.93**	**4.14**

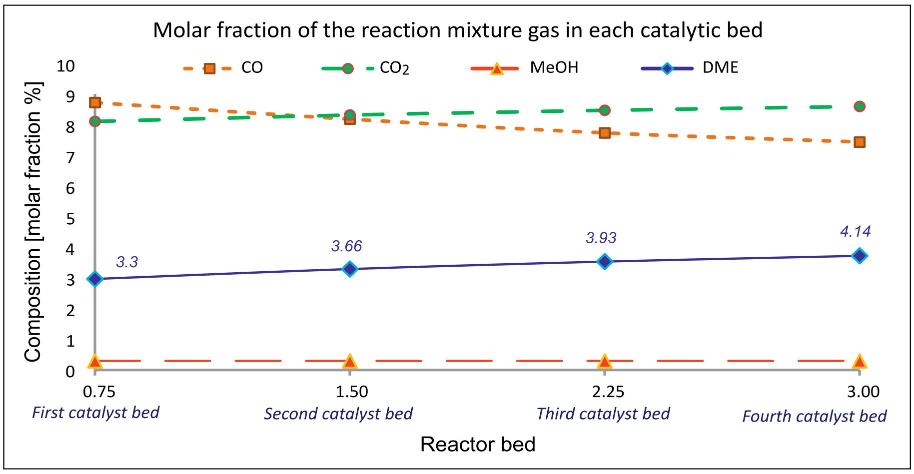

Figure 7. Concentration variations of components within all reactor beds following recirculation

Rysunek 7. Zmiany stężenia składników we wszystkich warstwach reaktora po recyrkulacji

Temperature variation in a multi-stage reactor for DME synthesis

Effective temperature management in a multi-stage reactor for dimethyl ether (DME) synthesis is crucial due to the exothermic nature of the reactions involved. Controlling these temperatures ensures optimal reactor performance and prevents thermal degradation of the catalytic materials. Cold gas injection between the catalyst layers is a key method for maintaining temperature control.

Temperature control and cold gas injection

The model developed in this study enabled precise determination of temperatures within each catalytic layer and the exact amount of cold gas, or quench gas, required to manage these temperatures effectively. Table 8 summarizes the temperatures at the inlets and outlets of each catalytic bed, as along with the corresponding cold gas flow rates.

Figures 8 and 9 provide graphical representations of the temperature data. Figure 8 depicts temperature fluctuations

Table 8. Temperature and gas mixture flow rate for each of the four beds

Tabela 8. Temperatura i natężenie przepływu mieszaniny gazów dla każdego z czterech złóż

Catalytic bed	Inlet flow [K mole/h]	Inlet temperature [°C]	Outlet flow [K mole/h]	Outlet temperature [°C]	Quench flow [K mole/h]	Quench temperature [°C]
1	6200	240.0	8532	359.8	2480	70
2	8179	279.0	9919	332.0	2480	70
3	10390	245.0	11740	328.3	1240	70
4	11270	303.1	13330	328.0		

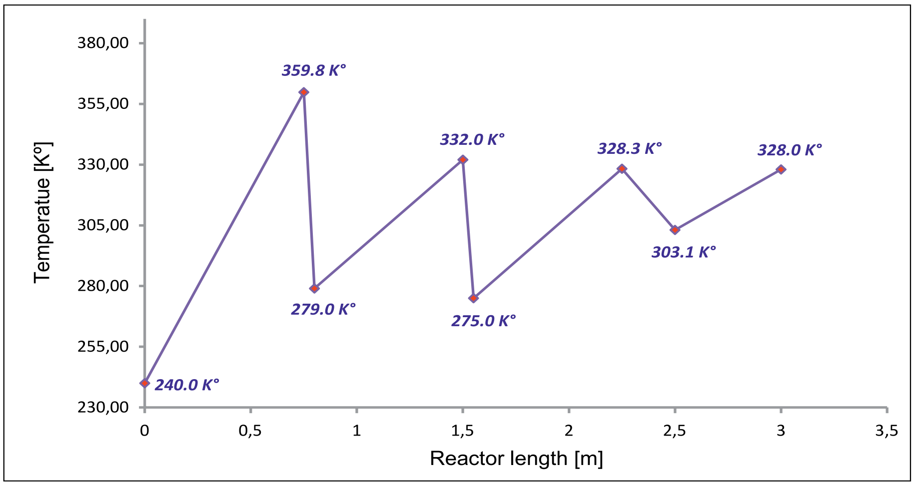

Figure 8. Temperature evaluation along the catalytic reactor

Rysunek 8. Ocena temperatury w reaktorze katalitycznym

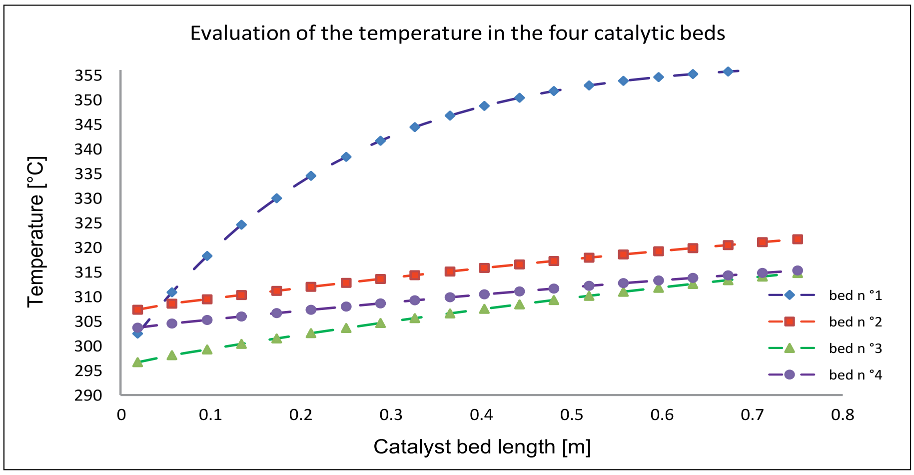

Figure 9. Temperature variations across the catalytic beds

Rysunek 9. Zmiany temperatury w warstwach katalitycznych

at the inlet and outlet of each layer along the reactor length, while Figure 9 illustrates temperature variations across each catalytic bed.

Analysis of temperature data

Analysis of Table 8 and Figure 6 reveals that the temperature at the outlet of the first catalytic bed reached approximately 360°C. To manage this, a substantial cold gas injection (2480 K mole/h) was required between the first and second layers. This amount of cold gas was also used between the second and third layers, reducing the temperature to around 270°C. Between the third and fourth layers, the cold gas flow was reduced to 1240 K mole/h, indicating a decrease in thermal intensity in the later stages.

- Comparison with methanol synthesis: The results show that DME synthesis requires significantly more cold gas than methanol synthesis. In methanol synthesis, the cold gas flow required to manage temperatures did not exceed 1991 K mole/h across the four catalytic layers, emphasizing the more exothermic nature of DME synthesis compared to methanol synthesis.
- Cooling gas strategy: To address temperature control in DME synthesis, we increased the proportion of cooling gas. At the reactor inlet, the total synthesis gas was split into 50% for cooling and 50% for heating before being introduced into the reactor. This strategy differs from methanol synthesis, where 40% of the gas is used for cooling and 60% for feeding the reactor.
- Reactor efficiency dynamics: The efficiency of the multilayer catalytic reactor varies across its layers. As illustrated in Figure 10, the initial layer exhibits higher efficiency due to the high concentration of reactants in the feed gas, which leads to a higher concentration of the product. Additionally, the exothermic nature of the DME synthesis reaction causes a significant temperature increase in the first layer, as shown in Figure 9.

As the reactant gas progresses through the subsequent layers, the concentration of reactants decreases while product

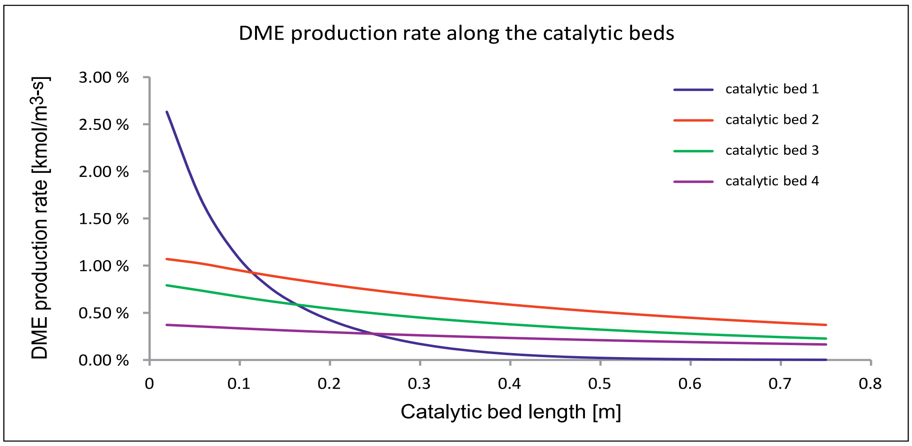

Figure 10. Variation of DME production rate along the catalytic beds

Rysunek 10. Zmienność tempa produkcji DME w reaktorze katalitycznym concentrations increase. This shift leads to a gradual decline in reaction efficiency and yield in later layers. Despite the high reactant concentrations in the cold gas injected between layers, its quantity is lower than the feed gas entering the first layer.

Precise temperature control in the multi-stage reactor is essential for successful DME synthesis. Effective temperature management requires substantial cold gas injection to maintain optimal temperatures between catalytic layers, reflecting the exothermic nature of the reaction. A thorough understanding of reaction characteristics and cooling requirements will enhance reactor design and operation, ultimately improving production efficiency.

Conclusion

In this study, we successfully demonstrated the feasibility of repurposing existing methanol production infrastructure for the synthesis of dimethyl ether (DME) using the CP1Z complex in Arzew. By employing Aspen HYSYS V-11 for process simulation, we effectively modeled and optimized the DME production process under realistic conditions.

Our study employed a bifunctional catalyst system comprising $CuO/ZnO/Al_2O_3$ for methanol synthesis and γ-alumina for methanol dehydration. This catalyst system effectively facilitated the reaction mechanism, leading to substantial DME production. Simulation results illustrated a progressive increase in DME concentration across the four catalytic beds, achieving 2.81% in the fourth bed and 4.14% after recycling. The incorporation of a recycling process for unconverted synthesis gas and unreacted methanol significantly enhanced the DME yield. These findings underscore the potential of traditional methanol reactors for efficient DME synthesis.

Temperature control emerged as a critical factor in reactor performance due to the highly exothermic nature of dimethyl ether (DME) synthesis reactions. To address this issue, we increased the amount of synthesis gas directed for cooling at the reactor inlet and subsequently injected it between the catalytic layers. This strategy proved effective in maintaining optimal reaction temperatures, preventing catalyst degradation, and enhancing DME productivity. Our modeling using aspen-HYSYS provided clear insights into the temperature variations throughout the reactor, enabling us to estimate the precise amount of cold gas required for the reactor's thermal management. Furthermore, this approach highlights the importance of simulation in balancing cold gas flow and controlling temperatures to ensure stable operation.

In conclusion, this research presents a comprehensive analysis and successful simulation of DME production using existing methanol production infrastructure. The findings offer a promising pathway for optimizing DME synthesis processes, contributing to the development of efficient and sustainable chemical production methods. Future work may focus on refining catalyst formulations and exploring alternative cooling strategies to further enhance reactor performance and product yield.

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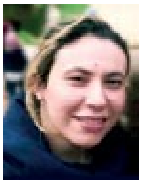
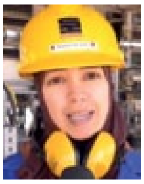
Prof. Ahmed FEDDAG, Ph.D.
Professor at the Department of Process Engineering
Abdelhamid Ibn Badis University
Route Balhacel, Mostaganem (UMAB), 27000 Algeria
E-mail: *feddam@yahoo.fr*



Ilhem SIDI-YACOUB, Ph.D.
Assistant Professor at the Department of Process Engineering
Abdelhamid Ibn Badis University
Route Balhacel, Mostaganem (UMAB), 27000 Algeria
E-mail: *Ilhem.s.y@gmail.com*



Ikram KHELIFA, Ph.D.
Process Engineer
Study and Development Department – GL3Z Gas Liquefaction Complex
B.P N 807, Arzew-Oran, 31200 Algeria
E-mail: *ouldsaidwidad@yahoo.fr*