

Thermodynamic Analysis of Glycerol Dry Reforming to Hydrogen at Low Pressure

Zaki Yamani Zakaria, Norshafika Yahya, Mazura Jusoh and Nurul Farhana Jamaluddin

Abstract—Hydrogen can be produced using several reforming methods from the byproduct of biodiesel which is glycerol. In this investigation, thermodynamic study for glycerol dry reforming to hydrogen at low pressure and different CO₂ to glycerol ratio (CGR) was carried out. Dry reforming of glycerol involves series of reactions and depends on several process variables such as pressure, temperature and ratio feed of the reactants. As for that, a thermodynamic equilibrium analysis has been performed by using direct minimization Gibbs energy method via the utilization of Matlab software. The process parameters considered in this study are temperature (573K-1273K), pressure (1, 0.5, 0.1, 0.05 and 0.01 atm) and CGR (1:1, 3:1, 6:1, 1:3 and 6:1). The result inferred that optimum conditions for hydrogen production can be attained when temperature = 1273K (higher), CGR = 1:6 (lower), pressure 0.01 atm (lower). CO showed almost similar trend to hydrogen formation, whereas CO₂ and H₂O showed different trend due to the effects of complex reaction network within the glycerol dry reforming process. The region for carbon suppression was also identified in order to avoid coking that could poison any possible catalyst involvement.

Keywords—thermodynamic, dry formation, glycerol, hydrogen, low pressure

I. Introduction

Biodiesel has been regarded as precious renewable alternative source to power up vehicles due to its environmentally friendly properties. Presently, development in various segments, especially in technology and innovation of vehicle without any details specification will all lead to the dissemination of hazardous pollutant that might destroy the environment. In order to minimize pollution release to the environment, biodiesel has been developed and chosen as the replacement for more harmful non-renewable fuel. Since biodiesel fuel have various advantages such as alternative of petroleum based fuel, renewable fuel, lower hazardous emissions of CO and CO₂ compared to regular diesel and nontoxic fuel, biodiesel have drawn many attention recently over the world [1].

The by-product of biodiesel production is crude glycerol, a product that is considered as potential candidate feed for clean hydrogen formation. Glycerol, co-produced via transesterification process in the biodiesel production is unwanted compound when it is in excess. Generally, high crude oil price has made biodiesel compatible in cost with petroleum diesel. To make biodiesel economically competitive to regular diesel at the present stage, one can opt to develop technologies to improve the utilization of crude glycerol into higher value added product such as hydrogen [2].

Besides effort to convert glycerol to hydrogen, main existing application of glycerol are directed to food additives, health care, polymer and pharmaceutical. However, the process is significantly restricted unless an energy-intensive purification step is previously carried out [3].

Hydrogen production from biomass such as glycerol has attracted great interest because of the potential application in fuel cells [4]. Hydrogen fuel cells offer high efficiency of energy conversion and known as one of the environmental friendly energy source. Hydrogen is widely used in the chemical and petroleum industries, and known as promising clean energy for electrical power generation and fuel devices components. Other than that, glycerol also may produce hydrogen gases as the alternative energy nowadays. The production of hydrogen for fuel cells, which are means of converting chemical energy into electrical energy known “clean” energy [5]. There are several methods that widely used for hydrogen production such as steam reforming, dry reforming and others.

Thermodynamics analysis of glycerol reforming for hydrogen production have been widely studied. This include the study of various important chemical reactions, different operating temperatures, pressures and feed ratios. [6, 7]. However, to the best of our knowledge, the thermodynamic investigation of glycerol dry reforming to hydrogen at low pressure is not been published yet. Hence, thermodynamic analysis using computing method will be performed. Thus, parameters such as temperature, pressure and feed ratios, in this case CO₂ to glycerol ratio (CGR) will be manipulated for comparing the number of moles for hydrogen and production of other imperative gases. The objectives of this research is to perform thermodynamics analysis of hydrogen and other gases component formation from the dry reforming of glycerol at a low pressure by using the direct minimization of the Gibbs free energy. It will be carried out by computing the equilibrium composition of synthesis gas.

II. Methodology

A. Gibbs Free Energy

Gibbs free energy is the most commonly used function for identifying the equilibrium state. To calculate the equilibrium composition of any reaction products in a system, the minimization of total Gibbs free energy method was employed.

The minimization of total Gibbs free energy function for the system is given using Eq. (1) as followed:

$$G^t = \sum_{i=1}^N n_i \bar{G}_i = \sum_{i=1}^N n_i \mu_i = \sum n_i G_i^0 = RT \sum n_i \ln \frac{f_i}{f_i^0} \quad (1)$$

Zaki Yamani Zakaria, Norshafika Yahya, Mazura Jusoh and Nurul Farhana Jamaluddin

Faculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Malaysia.

If the temperature and pressure of the system are constant, the equilibrium function of system as Eq. (2) is followed.

$$dG = \sum_{i=1}^K \mu_i dn_i \quad (2)$$

The objective to find set of n_i which minimize value of G and this can be solve using another two ways which are (i) stoichiometric; and (ii) non-stoichiometric.

Processing parameters varied are carbon dioxide to glycerol ratio (CGR) (1:1, 3:1, 6:1, 1:3 and 1:6), temperature (573K-1273K) and operating pressure (1, 0.5, 0.1, 0.05 and 0.01 atm). The possible products from this glycerol dry reforming at low pressure include hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO), water (H_2O) and carbon (C).

III. Result and Discussion

The thermodynamic study only considers the primary products from the C, H, O system, which include H_2 , CO, CO_2 , CH_4 and H_2O in gas phase and C in solid phase. The main possible reactions which may take place in glycerol dry reforming at low pressure are summarized in Table 1.

A. Hydrogen Production

Fig. 1 illustrates the number of hydrogen moles produced at different temperature and CGR at 1 atm. As can be seen, the number of hydrogen moles produced increases with increasing temperature. Number of hydrogen moles with CGR 1:6 is higher than CGR 6:1. This occurred when more hydrogen atoms are available from glycerol for the formation of hydrogen gas. Besides that, towards CGR 6:1, higher CO_2 feed will reduce the capacity of hydrogen production [7]. As can be seen in Fig. 1, when temperature is low (573K - 773K) number of hydrogen moles produced is very low, about only 0 to 1 moles. The production of hydrogen can be explained by reaction 4 and 5 from Table 1. The reactions show that, the higher the reaction temperature, more hydrogen is produced. Apart from that, reaction 2 and 3 also explained that as the temperature increase, the reaction will shift to the left.

The formation of hydrogen at varied low pressure at CGR 1:1 is shown in Fig. 2. No previous studies were found to investigate the thermodynamic analysis of glycerol dry

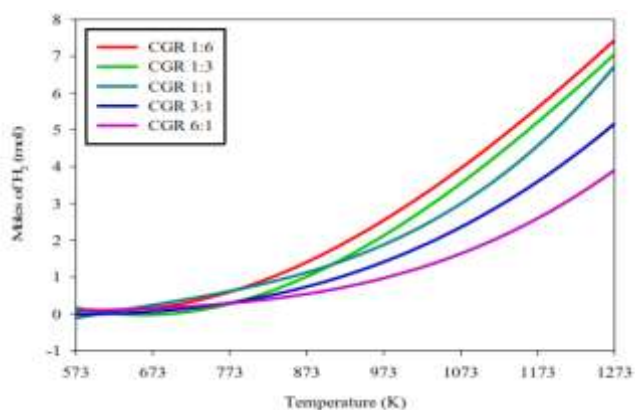


Figure 1. Moles of H_2 formation as a function of CGR and pressure at 1 atm.

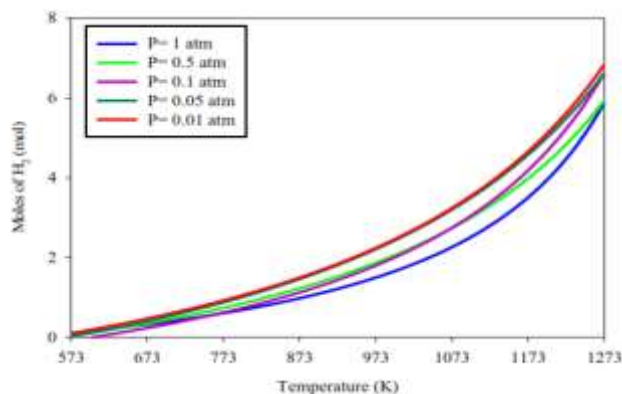


Figure 2. Moles of H_2 formation as a function of low pressure at CGR 1:1.

reforming to hydrogen at low pressure. However, there were reports on glycerol steam reforming at pressure higher than 1 atm. Their results show that the number of hydrogen moles decreased as the pressure increased [8]. Fig. 2 shows the number of moles hydrogen increased when temperature increasing. It can be seen that moles of hydrogen is slightly higher when pressure is lower, at temperature 773K and below. Above 773K, the effect of lower pressure begin to show some level of significance. This scenario indicated that hydrogen formation is optimum when temperature is higher and pressure is lower.

B. Carbon Dioxide and Carbon Monoxide Production

The profile of CO_2 formation at different CGR, different temperature, at 1 atm pressure is shown in Fig. 3. Moles of CO_2 at equilibrium reach maximum between temperature 673K to 773K for the CGR 1:6, 1:3 and 6:1. This can be described by reaction 3, 4 and 5 from Table 1. Reaction 3 and 4 reached optimum CO_2 formation at 773K. As temperature increase, the reaction shifted to the left thus explaining why CO_2 is being consumed and decreasing. Fig. 4 illustrates the formation of CO_2 at varied low pressure. Like H_2 formation trend, more CO_2 are formed when pressure is lowest. However, unlike H_2 formation trend, the CO_2 growth are not encouraged by temperature increase.

Fig. 5 shows the moles of CO at different low pressure at CGR 1:1. Moles of CO increase with the increasing of temperature and decreasing of pressure. The trend is almost comparable to that of H_2 formation trend.

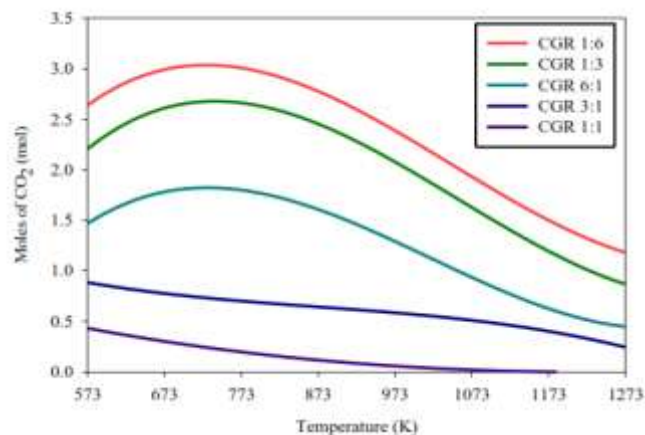


Figure 3. Moles of CO_2 formation as a function of CGR at pressure 1 atm

TABLE I. LIST OF POSSIBLE CHEMICAL REACTION

No. of reactions	Possible reactions	ΔH_{298} (kJ/mol)
1	$C_3H_8O_3 \leftrightarrow 4H_2 + 3CO$	251.18
2	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206.11
3	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-164.94
4	$CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO$	247.28
5	$CO + H_2O \leftrightarrow H_2 + CO_2$	-41.17
6	$C + H_2O \leftrightarrow H_2 + CO$	131.26
7	$C + 2H_2O \leftrightarrow 2H_2 + CO_2$	90.09

The number of CO moles at pressure 0.01 atm is higher than pressure 1 atm. This shows that at low pressure, more CO tend to be formed. The moles of CO produced at 1273K and 0.01 atm is approximately 10 moles, which is quite high and may negatively affect the environment. This phenomenon can be explained from reaction 1 and 4 as tabulated in Table 1.

Fig. 6 demonstrates the moles of CO at different CGR at 1 atm. CO moles formation increased when temperature and CGR inclined. At lower CGR (1:1) moles of CO is low but increases gradually with temperature. This can be related with reaction R1 from Table 4.1 that each produces 3 mol of CO when 1 mol glycerol reacted.

C. Methane and Water Production

CH_4 is not a desirable side product in H_2 and synthesis gas production. However, it can be useful for the oxidative coupling of methane (OCM) process [9] or oligomerization of hydrocarbons monomers [10]. Hence, it is still imperative to comprehend the trend of CH_4 formation via glycerol dry reforming. Fig. 7, shows that moles of CH_4 formation at various CGR, at 1 atm. Moles of CH_4 decrease with temperature increase. According to Wang et al [7], high temperature and CGRs, can inhibit the production of CH_4 . This is due to the fact that CH_4 is been consumed to react to form other gases. This can be explained from reaction R4 in Table 4.1. Maximum moles of CH_4 is produced at temperature 573K at CGR 1:6 is about 0.9 mol.

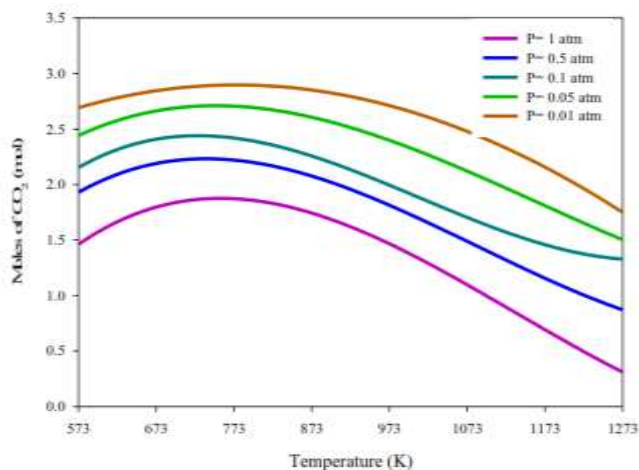


Figure 4. Moles of CO_2 as a function pressure at CGR 1:1.

Inversely, less than 1 mol of CH_4 is formed at 1273K. Fig. 8 shows moles of CH_4 formation at different pressure at CGR 1:1. Higher moles of CH_4 is formed at 1 atm. It is different than other gas components that give lower yield when at approaching vacuum condition. At the moment it is unexplained as why higher moles of CH_4 is favoured at 1 atm. Fig. 9 shows the moles of H_2O formation with different CGR at 1 atm. Moles of H_2O decrease when temperature increase. However, for CGR 1:6, 1:3 and 3:1, moles of H_2O slightly increase at 1073 K. This trending can be explained from reaction 5, 6 and 7 in Table 1.

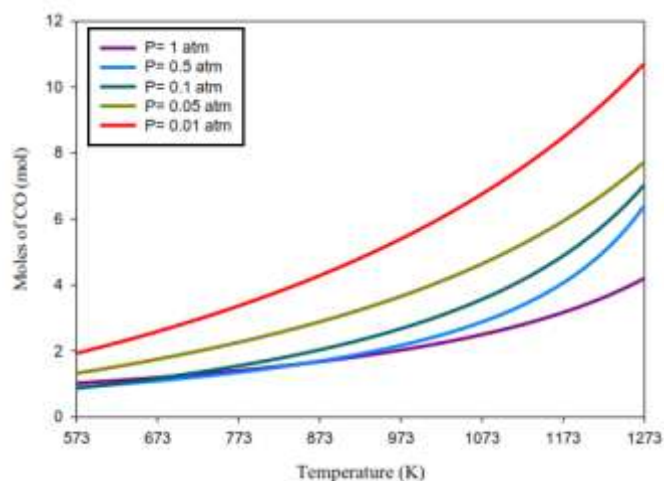


Figure 5. Moles of CO at different pressure at CGR 1:1.

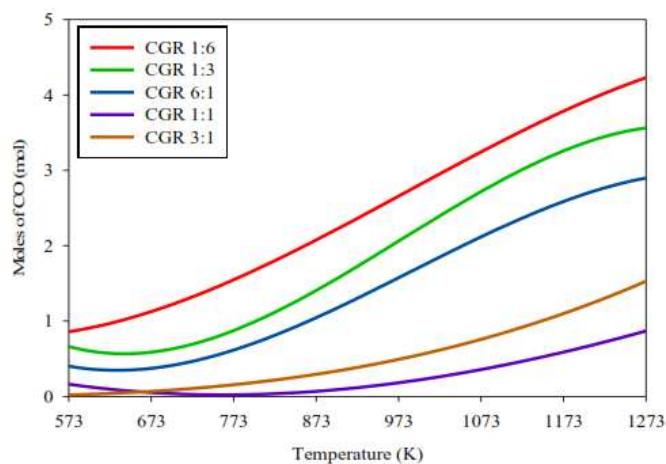


Figure 6. Moles of CO at different CGR at P=1 atm.

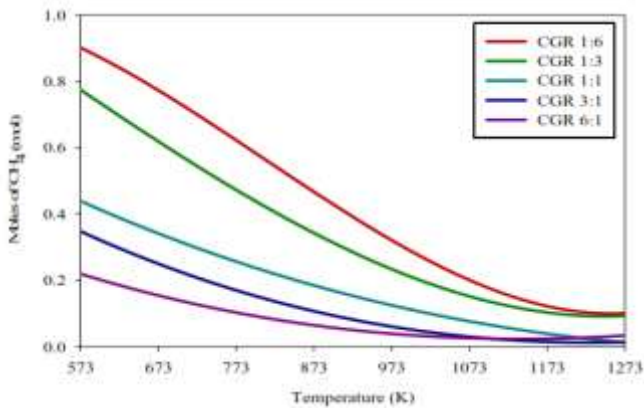


Figure 7. Moles of CH₄ as a function CGR at pressure 1 atm.

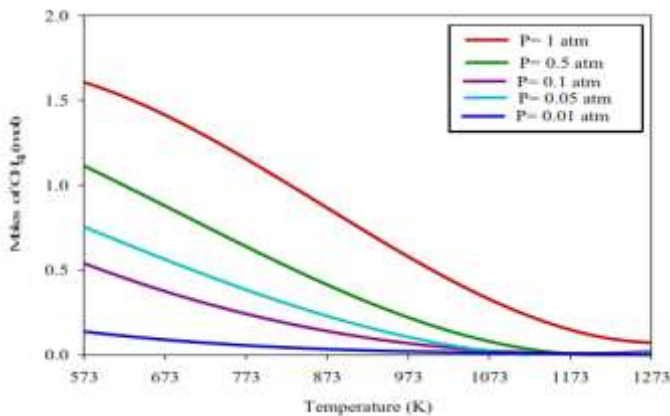


Figure 8. Moles of CH₄ as function pressure and CGR 1:1.

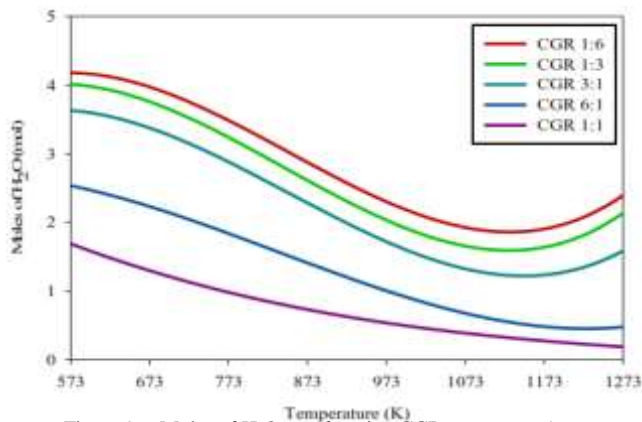


Figure 9. Moles of H₂O as a function CGR at pressure 1 atm.

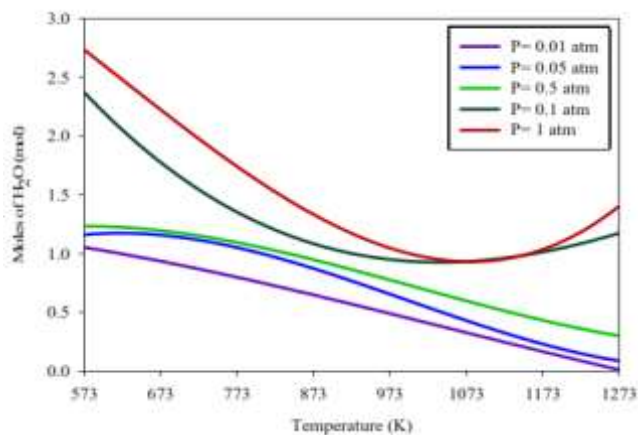


Figure 10. Moles of H₂O as a function of pressure at CGR 1:1.

Based on all of these reactions, it can be deduced that H₂O is being consumed as a reactant to form other components. Fig. 10 shows the moles of water with temperature at different pressures at CGR 1:1. As can be seen, the lower the pressure, the yields of H₂O decrease. The result for the lowest pressure 0.01 atm shows that the moles of water produced are decreasing and at temperature 1273K, the moles of water produced are approximately zero.

D. Carbon Formation

Fig. 11 shows the number of moles for carbon at different temperatures and CGR. Carbon formation is suppressed at higher temperatures and this clearly indicates that its formation can be avoided, thus minimizing the effect of catalyst poisoning. The trend also shows that the moles of carbon increase when the CGR increases, especially within the lower temperature region. This finding is critical since the formation of carbon is an undesired product in glycerol dry and steam reforming reactions.

Fig. 12 shows carbon formation with different pressures at CGR 1:1. It can be deduced that carbon formation is hindered at lower pressures and higher temperatures. Most importantly, it can be construed that carbon can be avoided when running the reaction at 1073K and above for the pressure range defined within this investigation. It is crucial not to run the reaction at 1 atm, in the context of this study, since carbon in its solid phase form could be most stable at this pressure.

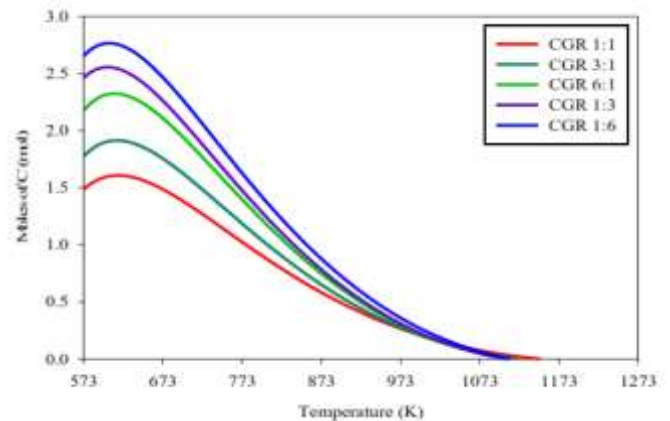


Figure 11. Moles of C as a function of CGR at pressure 1 atm.

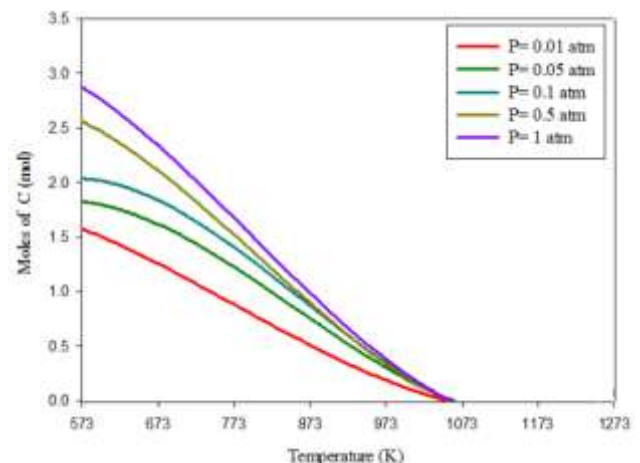
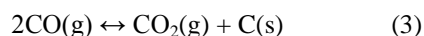


Figure 12. Moles of C as a function of pressure at CGR 1:1.

These carbon formation reactions are easily influenced by operational parameters due to their relatively lower equilibrium constants [11]. It can be observed from Fig. 11 and 12 that disproportionation reaction, notably known as *Boudard* reaction (Eq. 3) is predominant. The existence of carbon can poison catalysts in reforming reactions. However, as can be observed, no carbon is produced under conditions which are optimized for hydrogen production for dry reforming. The amount of solid carbon determined from experiments is usually larger than that from thermodynamic analysis. This is mainly due to the fact that once carbon is formed it is readily accumulated.



IV. Conclusion

Thermodynamic analysis of glycerol dry reforming to hydrogen and other important gases at low temperature has been performed by employing Gibbs free energy minimization method which were obtained using Matlab software. The effects of pressure, temperature and CGR have been studied. Maximum H_2 is formed with increase in temperature, lower pressure (0.01 atm) and CGR 1:6. Higher pressure and higher CGR inhibit the formation of H_2 . Similar trend could be observed for CO , while, CH_4 and H_2O it showed inverse trend. Under optimum condition to yield maximum hydrogen, carbon formation is suppressed, thus diminished the chances of potential catalyst deactivation

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About Author (s):



Ir. Dr. Zaki Yamani Zakaria has been with the Faculty of Chemical Engineering since 2008. His main research interests are in catalytic reaction engineering, engineering education and green related technology.