A Comparative Thermodynamic and Experimental Analysis on Hydrogen Production by Steam Reforming of Glycerin

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Glycerin production has soared with the increase in biodiesel production in recent years. One possibility of using this excess glycerin is in hydrogen production. Steam reforming of glycerin for hydrogen production involves complex reactions. As a result, several intermediate byproducts are formed and end up in the product stream, affecting the final purity of the hydrogen produced. Furthermore, the yield of the hydrogen depends upon several process variables, such as the temperature, ratio of reactants, and system pressure. In this study, a thermodynamic equilibrium analysis coupled with experimentation has been performed for the steam-reforming process of glycerin over the following variable ranges: pressure of 1−5 atm, temperature of 600−1000 K, and water/glycerin feed ratio of 1:1−9:1. The equilibrium concentrations of different compounds were calculated by the method of direct minimization of the Gibbs free energy. The study revealed that the best conditions for producing hydrogen are as follows: temperature of >900 K, atmospheric pressure, and a molar ratio of water/glycerin at 9:1. Under aforementioned conditions, methane production is minimized and the carbon formation is thermodynamically inhibited. Experimental results over the Ni/MgO catalyst were compared against the results obtained from thermodynamic analysis.

1. Introduction

Although the role of liquid fuels produced from biomass is minuscule in the total energy supply, their production and demand is increasing worldwide. Biodiesel production, for example, has increased from 0.5 million gallons in 1999 to 250 million gallons in 2006 in the United States alone.[1] With the ever-increasing production of biodiesel, a glut of glycerin ($C_3H_8O_3$) is expected in the world market. Currently, glycerin is used in many applications but mainly on personal care, food, oral care, tobacco, and polyurethane production. The purification of crude glycerin from the biodiesel plants is a major issue. Increasing production of biodiesel will saturate the glycerin market if other alternative uses of glycerin are not found. The glycerin price has already dropped by two-thirds in the last 5 years because of surplus amounts in the market. It is prudent to explore alternative uses of glycerin; one possibility is using it as a source for hydrogen production.

A few studies have been conducted on glycerin reforming for hydrogen production. Dumesic and co-workers[2−4] produced hydrogen from biomass-derived oxygenated hydrocarbons, including glycerin, in an aqueous-phase-reforming (APR) process. Czernik and co-workers[5] produced hydrogen via steam reforming of crude glycerin using a commercial nickel-based naphtha-reforming catalyst (C11-NK). Recently, other studies[6−8] reported the performance of noble metal-based catalysts for glycerin reforming.

The overall reaction of hydrogen production by steam reforming of $C_3H_8O_3$ is given as

$$C_3H_8O_3\ (g) + 3H_2O\ (g) \rightarrow 7H_2\ (g) + 3CO_2\ (g) \qquad (1)$$

Although limited studies on glycerin reforming for hydrogen production have appeared, a detailed thermodynamic analysis has not yet been carried out. Steam reforming of glycerin for hydrogen production involves complex reactions. As a result, several intermediate byproducts are formed and end up in the product stream, affecting the final purity of hydrogen produced. Furthermore, the yield of hydrogen depends upon several process variables, such as the system pressure, temperature, and water/glycerin feed ratio (WGFR). The first step toward understanding the effects of the aforementioned variables is a complete thermodynamic analysis. From this study, ideal reaction conditions that maximize hydrogen yield and minimize the undesirable products

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can be determined. It should be noted that a thermodynamic analysis does not consider the reaction kinetics. However, the results from the thermodynamic analysis could be used as a benchmark to compare the results from experimental studies.

The aim of this study is to analyze the production of hydrogen and other compounds with varying process variables (temperature, pressure, and WGFR). The equilibrium concentrations of different compounds were calculated by direct minimization of the Gibbs free energy, *G*. This analysis has been performed for the steam-reforming process of glycerin over the following variable ranges: pressure of 1−5 atm, temperature of 600−1000 K, and WGFR of 1:1−9:1. Experimental studies have been carried out over a Ni/MgO catalyst and compared with the results from the thermodynamic analysis.

2. Methodology

2.1. Thermodynamic Analysis. If the pressure and temperature of the system are constant, the equilibrium of the system is given as follows:[9]

$$\mathrm{d}G = \sum_{i=1}^{K} \mu_i \, \mathrm{d}n_i \tag{2}$$

The objective is to find the set of n_i values that minimize the value of *G*. This can be solved in two ways:[10] (i) stoichiometric and (ii) nonstoichiometric thermodynamic approaches. In the stoichiometric approach, the system is described by a set of stoichiometrically independent reactions, and they are typically chosen arbitrarily from a set of possible reactions.[11] On the other hand, in a nonstoichiometric approach, the equilibrium composition is found by the direct minimization of the Gibbs free energy for a given set of species.[12] The advantages of the nonstoichiometric approach over the stoichiometric approach are as follows:[13] (a) a selection of the possible set of reactions is not necessary; (b) no divergence occurs during the computation; and (c) an accurate estimation of the initial equilibrium composition is not necessary. The nonstoichiometric approach has been used in this study.

From eq 2, we can write

$$G = \sum_{i=1}^{K} \mu_i n_i \tag{3}$$

To find the n_i value that minimizes the value of *G*, it is necessary that the values of n_i satisfy the elemental mass balances, i.e.,

$$\sum_{i=1}^{K} a_{li} n_i = b_l, \quad l = 1, ..., M \tag{4}$$

Equation 3 can be further expressed as[12,14]

$$G = \sum_{i=1}^{K} n_i \Delta G_i^0 + RT \sum_{i=1}^{K} n_i \ln y_i + RT \sum_{i=1}^{K} n_i \ln P \tag{5}$$

At low pressure and high temperature, the system can be considered as ideal.[12,14] The objective function (eq 5) is minimized using Mathcad version 11.[15] It is also solved by Lagrange's multiplier method using Mathcad version 11 while satisfying the elemental mass balances as given in eq 4. The results are found to be the same from both methods. We considered the possible products from glycerin steam reforming to be hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), unreacted water and $C_3H_8O_3$, and carbon (C),[6−8,16] although small traces of ethylene, ethane, or other alkanes are produced during the reaction. Three elements, carbon, hydrogen (H), and oxygen (O), are contained in all of the products considered in this study, and therefore, only C, H, and O are used for the elemental mass balance. Total Gibbs free energy is considered to be independent of carbon, because the free energy of formation of solid carbon is zero and it has no vapor pressure.[14] Therefore, carbon is included only in the elemental constraints but not in the objective function. As entry data, the program needs the pressure, temperature, number of compounds, number of atoms, values of the Gibbs free energy of formation, and initial guesses for n_i values in the equilibrium. Thermodynamic data were obtained from Lide,[17] Yaws,[18] and Rossini.[19]

2.2. Experimental Procedure. *Catalyst Preparation*. Ni catalysts were prepared over MgO supports purchased from Nanoscale Materials (Manhattan, KS). Catalysts were prepared by the wet impregnation method using nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] purchased from Sigma-Aldrich (St. Louis, MO). Ni loading was 15 wt %, and the catalysts were dried at 383 K for 12 h and calcined at 773 K for 6 h in air. Catalyst samples were sieved, and a 16−35 mesh fraction was used for the catalytic measurement.

Catalyst Performance Testing. Experiments were carried out in a tube furnace that could reach temperatures up to 1373 K. Glycerin and water were mixed in a separate container at a predefined glycerin/water molar ratio of 1:6. The mixture was introduced into the reactor using a high-performance liquid chromatography (HPLC) pump (LC, 20AT; Shimadzu Scientific Instrument, Columbia, MD) at 1.0 mL/min. Catalyst powder was placed in the middle of the reactor with quartz wool at two sides, and 1.5 g of catalyst was loaded during the test. Prior to the experiment, catalysts were reduced by using H_2 gas (50 mL/min) for 1 h. The reactor was made of a stainless-steel tube with a $^1/_2$ in. outer diameter and a 0.083 in. wall thickness and was purchased from Swagelok (Pelham, AL). The gas stream from the reactor was cooled using crushed ice and water. Unreacted water, glycerin, and other liquids formed during the reaction were collected for further analysis. Outlet gas was sent through a moisture trap before purging into the GC (GC6890; Agilent Technologies, Inc., Palo Alto, CA). H_2 content in the outlet gas was analyzed by a thermal conductivity detector (TCD) with a HP-Plot Molecular Sieve column. Concentrations of CO, CH_4, and CO_2 were analyzed by a flame ionization detector (FID) with a HP-Plot Q column. Both the detectors were set at

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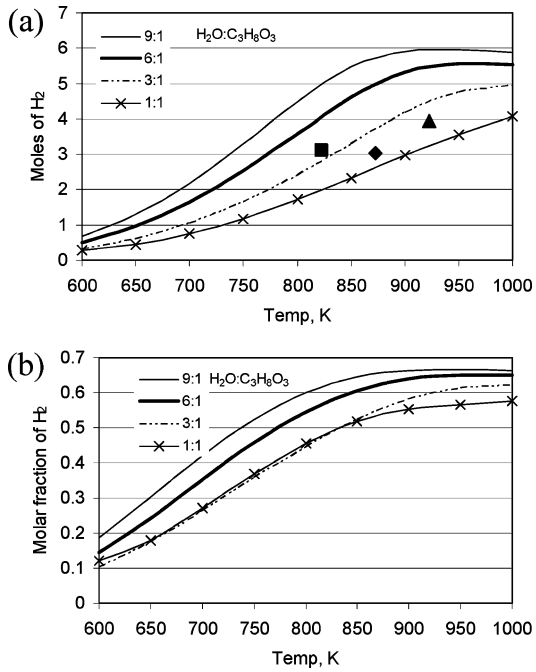

Figure 1. Thermodynamic analysis: (a) hydrogen moles versus temperature at different WGFRs at $P = 1$ atm and (b) mole fraction (dry basis) of hydrogen versus temperature at different WGFRs at $P = 1$ atm. Experimental analysis: (■) H_2 moles at 823 K, (◆) H_2 moles at 873 K, and (▲) H_2 moles at 923 K from the experiment.

523 K, and three replications were done for each measurement. Data presented in this paper are the average value from three replications.

3. Results and Discussion

The production of hydrogen and other compounds at different temperatures, WGFRs, and pressures have been analyzed on the basis of thermodynamic analysis. Over the temperature, pressure, and WGFR ranges analyzed, the conversion of glycerin was always greater than 99.99% and it can be considered that the conversion was complete. Our experimental results over Ni/MgO at 823−923 K showed that the glycerin conversion to gaseous products was ∼80% based on the carbon balance, although glycerin conversion was 100%.

3.1. Hydrogen Production. Figure 1 depicts the hydrogen moles and molar fraction at different temperatures and WGFRs. As can be seen from Figure 1a, the number of moles of hydrogen increases with an increasing temperature. A similar trend was observed over the Ni/MgO catalyst. The number of H_2 moles was increased from 3.1 to 4.0 while increasing the temperature from 823 to 923 K at a glycerin/water molar ratio of 1:6. The significant difference between the experimental results and the results from thermodynamic analysis is primarily due to the effect of catalysts. It is obvious from the experimental results that the catalyst prepared in our lab is not active enough to achieve thermodynamic equilibrium. Similarly, the number of moles of hydrogen increases with increasing WGFRs and decreasing pressure (see Figure 2a). The effect of the pressure on the glycerin steam-reforming process is found to be consistent with methanol and ethanol steam-reforming processes.[13,14,20] The highest quantity of hydrogen was produced with excess water at all temperatures. Accordingly, it was elucidated that the best

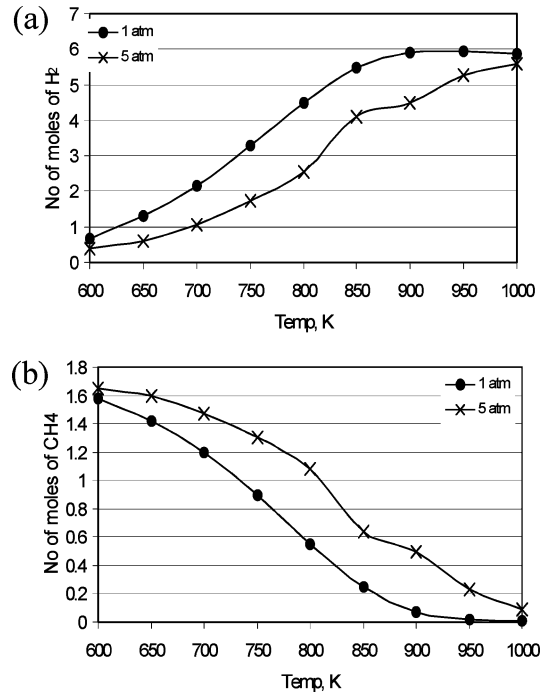

Figure 2. Thermodynamic analysis: (a) hydrogen and (b) methane moles produced at selected pressures and WGFR = 9:1.

conditions to produce hydrogen are with excess water. The upper limit of the moles of hydrogen produced per 1 mol of glycerin is 6 at 960 K, WGFR = 9:1, and $P = 1$ atm versus the stoichiometric value of 7. At higher WGFRs, i.e., 9:1 and 6:1, the number of moles of hydrogen produced at 1000 K is lower than at 950 K. The number of moles of hydrogen is at its maximum at 960 K and decreases thereafter in both cases. A similar observation was made by Semelsberger and Borup[21] in dimethyl ether steam reforming. Moles of hydrogen decrease together with CO_2 at temperatures >960 K, and at the same time, moles of CO and water increase. This can be attributed to the reverse water−gas shift reaction as given in eq 6. The equilibrium constant (K_p) of the water−gas shift reaction decreases as the temperature increases, meaning that a reverse water−gas shift is favored at higher temperatures. Figure 3 depicts the equilibrium constants for eqs 6−9.

$$CO\ (g) + H_2O\ (g) \leftrightarrow CO_2\ (g) + H_2\ (g) \qquad (6)$$

3.2. Methane Production. CH_4 competes against H_2, and obviously, CH_4 is not a desirable product if the ultimate goal is H_2 production. Figure 4 shows the moles of CH_4 and the CH_4 molar fraction as a function of the temperature. CH_4 production decreases when the temperature and the WGFR increased. However, a higher pressure favors the formation of CH_4 (see Figure 2b). Our experimental results also confirmed that the CH_4 formation decreased with an increase in temperature. About 0.64 mol of CH_4 was produced at 823 K and reduced to 0.56 mol by increasing the temperature to 923 K, with all other conditions remaining same. Thermodynamically, at higher WGFRs, i.e., 9:1 and 6:1, and at higher temperatures (>950 K), the formation CH_4 is almost inhibited. However, we could not achieve thermodynamic equilibrium with our catalyst. As the temperature increases, moles of water and CH_4 decrease

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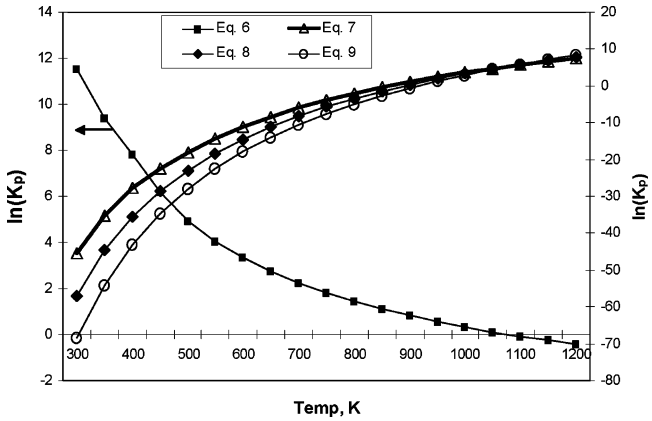

Figure 3. Equilibrium constants of the water−gas shift reaction and methane reforming versus temperature. K_p is determined from the Van't Hoff relation.

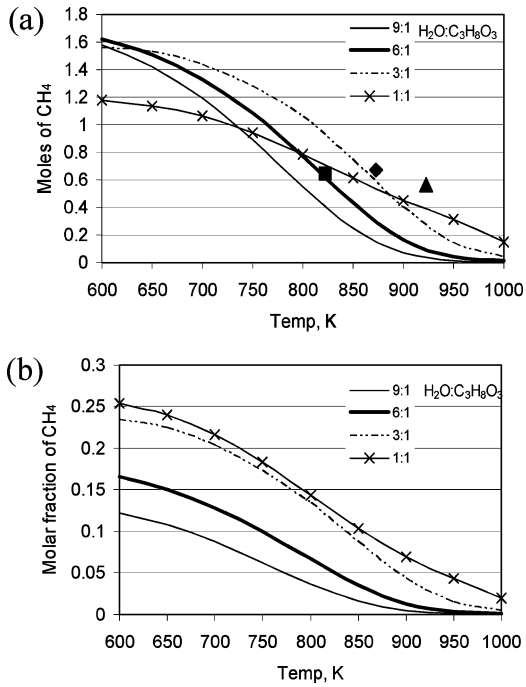

Figure 4. Thermodynamic analysis: (a) moles of methane versus temperature at different WGFRs at $P = 1$ atm and (b) mole fraction (dry basis) of methane versus temperature at different WGFRs at $P = 1$ atm. Experimental analysis: (■) CH_4 moles at 823 K, (◆) CH_4 moles at 873 K, and (▲) CH_4 moles at 923 K from the experiment.

with increasing CO, CO_2, and H_2. This is can be attributed to the methane steam reaction to produce CO or CO_2 and H_2 as given by the following equations:[20]

$$CH_4\,(g) + 2H_2O\,(g) \leftrightarrow CO_2\,(g) + 4H_2\,(g) \qquad (7)$$

$$CH_4\,(g) + H_2O\,(g) \leftrightarrow CO\,(g) + 3H_2\,(g) \qquad (8)$$

As can be seen from Figure 3, the methane steam reaction is favored at higher temperatures. However, at WGFR 1:1, the CH_4 formation is lower compared to other feed ratios analyzed in the study. This can be due to the significant amount of carbon formation (see Figure 6). Although, CH_4 formation is low at low WGFR, the molar fraction is higher than other feed ratios analyzed in the study. As can be seen from Figure 4b, as we increase the temperature and WGFR, the mole fraction of CH_4 decreases.

3.3. Carbon Monoxide and Carbon Dioxide Production. Oxygenated compounds CO and CO_2 are considered impurities

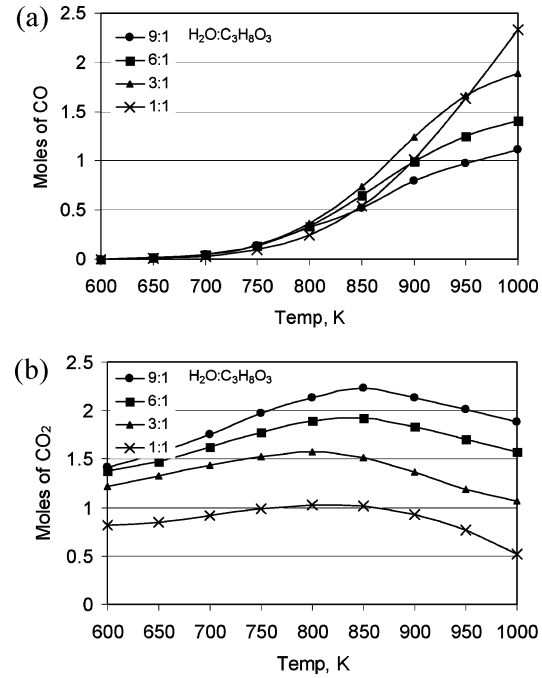

Figure 5. Thermodynamic analysis: (a) moles of CO versus temperature at different WGFRs at $P = 1$ atm and (b) moles of CO_2 versus temperature at different WGFRs at $P = 1$ atm.

because they do not compete against H_2. Figure 5 shows the number of moles of CO and CO_2 at different temperatures under selected WGFRs based on thermodynamic analysis. The number of moles of CO increases with the increase in the temperature but decreases with the increasing WGFR. However, the number of moles of CO_2 increases with an increasing temperature, goes through a maximum at around 850 K, and then decreases at higher temperatures. This behavior may be attributed to the reformation of CH_4 with CO_2 (eq 9).[22]

$$CH_4\,(g) + CO_2\,(g) \leftrightarrow 2CO\,(g) + 2H_2\,(g) \qquad (9)$$

3.4. Carbon Production. A catalyst is needed for the steam reformation of glycerin, and the knowledge of the conditions promoting carbon formation is essential. Otherwise, carbon will poison the catalysts. This information can be obtained from a thermodynamic analysis. Carbon deposition on the surface of the catalyst will result in several undesirable reactions and products affecting the purity of the reformation products. The formation of carbon will cause the loss of the effective surface area, lower the heat-transfer rate from the catalyst to gas, and plug the void space within the catalyst.[20] Carbon occurrence may arise because of the decomposition of CO or CH_4 or the reaction of CO_2 or CO with H_2.[13] The possible reactions that can be attributed to carbon formation are given as follows:

$$2CO\,(g) \leftrightarrow CO_2\,(g) + C\,(s) \qquad (10)$$

$$CH_4\,(g) \leftrightarrow 2H_2\,(g) + C\,(s) \qquad (11)$$

$$CO\,(g) + 2H_2\,(g) \leftrightarrow H_2O\,(g) + C\,(s) \qquad (12)$$

$$CO_2\,(g) + 2H_2\,(g) \leftrightarrow 2H_2O\,(g) + C\,(s) \qquad (13)$$

However, it should be noted that the thermodynamic analysis does not include the effect of the catalysts but gives the information under what conditions coke formation can be avoided. Figure 6 shows the range of the conditions under which

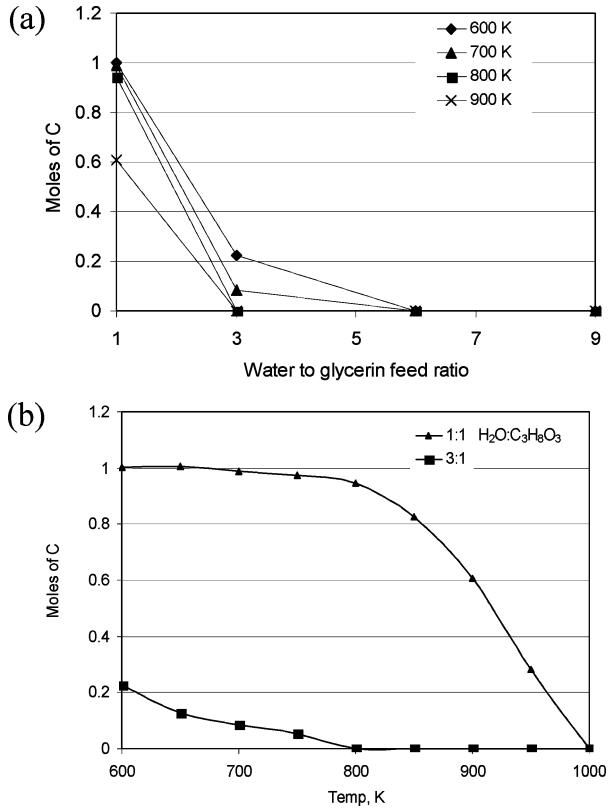

Figure 6. (a) Moles of carbon formation at different WGFRs at selected temperatures at $P = 1$ atm. (b) Moles of carbon formation at different temperatures at selected WGFRs at $P = 1$ atm.

the solid carbon formation is possible. At 1000 K, no carbon is formed at any WGFR. At WGFRs 6:1 and 9:1, carbon formation was thermodynamically inhibited at any temperature analyzed in this study. While increasing WGFRs from 1:1 to 3:1, carbon formation drops significantly.

5. Conclusion

A thermodynamic analysis followed by experimental verification for hydrogen production by steam reforming of glycerin has been performed. The number of moles of hydrogen produced is calculated on the basis of minimizing the Gibbs free energy. High temperatures, low pressures, and high WGFRs favor the hydrogen production. The study revealed that the best conditions for producing hydrogen are at a temperature of >900 K, a molar ratio of water/glycerin of 9:1, and a pressure of 1 atm. Under these conditions, methane production is minimized and carbon formation is thermodynamically inhibited. The upper limit of the moles of hydrogen produced per 1 mol of glycerin is 6 versus the stoichiometric limit of 7. The behavior of this system is very similar to that of steam reforming of ethanol. Experimental results are still far from thermodynamic equilibrium. This leaves room for finding the efficient catalyst for hydrogen production from glycerin.

Nomenclature

G = Gibbs free energy
T = Temperature
P = Pressure
n_i = Number of moles of species i
K = Total number of chemical species in the reaction mixture
R = Gas constant
μ_i = Chemical potential of species i
y_i = Mole fraction of species i
ΔG_i^0 = Standard Gibbs free energy of the formation of species i
N = Total number of moles of all species in the gas mixture
a_{li} = Number of gram atoms of element l in 1 mol of species i
b_l = Total number of gram atoms of element l in the reaction mixture
M = Total number of atomic elements

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