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A Thermodynamic Analysis of Glycerol Monostearate Production by Glycerolysis

D. D. Anggoro*, S. B. Sasongko, L. Buchori and B. U. Le Monde
Department of Chemical Engineering, Faculty of Engineering, Diponegoro University,
50275, Semarang, Central Java, Indonesia
*Corresponding author (e-mail: dididwianggoro@lecturer.undip.ac.id)

Thermodynamic analysis was performed on the reaction producing glycerol monostearate (GMS) from glycerol and stearic acid to examine the reaction's feasibility. Generation of GMS by glycerolysis of glycerol with stearic acid or fatty acids is thermodynamically advantageous in accordance with the equilibrium constant, K. Thermodynamic analysis was carried out to determine the parameters that affect the glycerolysis reaction using MATLAB 2014A and Microsoft Excel 2013. The obtained values of ΔH_r^o; $\Delta S_r^o$and ΔG_r^o were + 45.69 kJ/mol; +1.144 kJ/mol.K and –1.074 kJ/mol. Equilibrium constants at 433.15 K, 453.15 K, and 473.15 K for this synthesis were favourable, at 5.76 x 10^{24}, 1.43 x 10^{27} and 2.23 x 10^{29}, respectively. The higher the temperature, the greater the value of ln K, which suggests a limitless equilibrium. The largest yield of the substances involved in the reaction was obtained at 473 K with $C_3H_8O_3$ (0.2286 mol), $C_{18}H_{36}O_2$ (0.0620 mol), $C_{21}H_{42}O_4$ (0.4379 mol) and H_2O (0.27131 mol). Negative ΔG_r^o values for this reaction suggest that formation of glycerol monostearate ($C_{21}H_{42}O_4$) was plausible and feasible, and the formation of reaction products at equilibrium was highly favoured. This prediction provides an overview of the reaction to ensure an optimal yield of glycerol monostearate.

Key words: Thermodynamic analysis; equilibrium; glycerolysis; glycerol monostearate

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Glycerol or propane-1,2,3-triol is a colourless, odourless, thick liquid with a sweet taste, that is fabricated from natural or petrochemical raw materials. Glycerol has both hydrophobic and hydrophilic properties as its chemical structure contains three hydroxyl groups [1]. These molecular structures and physiochemical properties make it a functional and convertible compound that can be esterified with acid to obtain alternative derivative products [2].Glycerol monostearate (GMS) enhances each derivative product of glycerol, has a high economic value, and good market prospects. It consists of a hydrophilic head and a hydrophobic tail, thus it has detergency properties and can stabilize oil and water emulsions [3]. GMS is widely used as an emulsifier in the food, pharmaceutical, and cosmetic industries [4]. The esterification process is reversible, and the reaction remains limited by equilibrium. Consequently, the conversion of acids is limited by thermodynamic equilibrium. Acid conversion can be improved by identifying and modifying the reaction process parameters such as by adding a catalyst, changing the reaction temperature and paying attention to excess reactants in the reaction [5]. The most common process used to synthesize glycerol monostearate is by the reaction of stearic acid with glycerol and esterification, or reacting glycerol and triglycerides by transesterification [6]. These reactions are usually catalyzed with sulfonic acid, sulfuric acid and phosphoric acid [7].

In previous research, the synthesis of glycerol and stearic acid used a zeolite Y catalyst to produce glycerol monostearate. Zeolite Y with the highest total value and surface acidity was reacted with glycerol and stearic acid to obtain a GMS yield of 4% [8]. The yield of glycerol monostearate is strongly dependent on the chemical thermodynamics of the reaction. A high mole ratio of stearic acid to glycerol and high reaction temperatures appear to be advantageous in converting glycerol to glycerol monostearate, because esterification of glycerol with stearic acid is reversible and the mole ratio of stearic acid to glycerol can shift the chemical equilibrium. Thermodynamic analysis of the glycerolysis of glycerol and stearic acid to produce glycerol monostearate using esterification has not been previously reported. In this study, computational methods using MATLAB 2014A and Microsoft Excel 2013 were used to predict the reaction conditions of the glycerolysis and the yield of the product.

EXPERIMENTAL

Thermodynamic Analysis

Thermodynamic analysis of GMS production from glycerol and stearic acid is necessary to assess the reaction's feasibility. This study consists of several steps:

Calculation of the chemical equilibrium constant at standard conditions

The chemical equilibrium constants of reaction at standard conditions were calculated as follows. First, the change of standard molar enthalpy ΔH_r^0 and change of standard molar entropy ΔS^0 of this reaction were calculated using equations (1) and (2). The standard molar enthalpy of formation ΔH_f^0, and standard molar entropy (S) of all reactants and products in the equal phase involved in the reaction were obtained.

$$\Delta H_r^o = \Delta H_f^o \text{ product} - \Delta H_f^o \text{ reactant} \tag{1}$$

$$\Delta S_r^o = \Delta S^o \text{ product} - \Delta S^o \text{ reactant} \tag{2}$$

The standard molar Gibbs free energy change of the reaction was then calculated. By interpreting the negative and positive states, the degree of spontaneity can be estimated [9]. The standard Gibbs free energy change is an equation of temperature (T), enthalpy change (ΔH) and entropy change (ΔS), as below:

$$\Delta G_r^o = \Delta H_r^o - T \text{ x } \Delta S_r^o \tag{3}$$

Determination of the reaction equilibrium constant (K) at various temperatures

The equilibrium constant at different temperatures is determined by the following equation:

$$\frac{\Delta G}{RT} = \frac{\Delta Gr - \Delta Hr}{RT} + \frac{\Delta Hr}{RT} + \frac{1}{T}\int_{T0}^{T}\frac{\Delta Cp}{R}dT - \int_{T0}^{T}\frac{\Delta Cp}{R}\frac{dT}{T} \tag{4}$$

$$K = \exp(-\Delta G_r^o/RT) \tag{5}$$

The temperature dependence of the heat capacity of each component is given in Table 1, where the first integral is (8),

$$\frac{1}{T}\int_{T0}^{T}\frac{\Delta Cp}{R}dT \tag{6}$$

This integral can be solved with a computational program (MATLAB):

IDCPH (T0, T1, dA, dB, dC, dD)

The second integral is given by the analog equation (4),

$$\int_{T0}^{T}\frac{\Delta Cp}{R}\frac{dT}{T} \tag{7}$$

This integral can also be solved by computation (MATLAB):

IDCPS ((T0, T1, dA, dB, dC, dD)

Prediction of the equilibrium composition of the substances involved in the reaction at the different temperatures

This prediction was calculated using the quadratic equation for equilibrium to determine the unknown variable (9),

$$K = \frac{x_{GMS} \cdot x_{H_2O}}{x_{Gly} \cdot x_{SA}} \tag{8}$$

where x is the molar concentration.

Change the equation to a quadratic equation,

$$c - b\epsilon + a\epsilon^2 = 0 \tag{9}$$

$$K - 2K\epsilon + (K-1)\epsilon^2 = 0 \tag{10}$$

Finally,

$$\epsilon_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{11}$$

Minimization of Gibbs Energy and Prediction of Equilibrium Composition of Reaction Substances

The difficulty in minimizing the Gibbs free energy was revealed by the atomic fraction based on the basic principles of thermodynamics. A feasibility analysis of the minimization problem was carried out to identify the optimal conditions [12] when the system reached equilibrium at the relevant T and P, and the Gibbs energy-minimizing composition of each component in the mixture [13]. In a closed reaction system, each mole number of atoms is fixed during a chemical reaction. The number of moles of a particular atom present in all chemical species in any chemical reaction must equal the initial mole number of that atom - minimized by including boundary conditions in the objective function. The boundary condition is the number of atoms required in the reaction based on appropriate references where there are three atoms, namely C, H, and O [14]. The number of moles of the three atoms is included in the objective function using Lagrange Multipliers λ_1, λ_2 dan λ_3 in the equation below [15].

$$\sum_{i=1}^{N-1} n_i \left(\Delta G_{fi}^0 + RT\ln\frac{y_i \Phi_i P}{P^0} + \sum \lambda_k a_{ik}\right) \qquad (12)$$

RESULTS AND DISCUSSION

Standard enthalpy (ΔH^o_r), entropy (ΔS^o_r) and Gibbs free energy change (ΔG^o_r) of reaction

The synthesis of glycerol monostearate by reaction of glycerol and stearic acid involves chemical structure rearrangement and affects the energy of the reaction system. This can be observed from ΔH_r^o, ΔS_r^o and ΔG_r^o. In thermodynamic analysis, Excel and MATLAB programs can be used to obtain values for ΔH_r^o, ΔS_r^o and ΔG_r^o .

From equation (1), (2) and (3), the values obtained for ΔH_r^o and ΔS_r^o were +45.69 kJ/mol, +1.144 kJ/mol.K and –1.074 kJ/mol, respectively. Even though the value of ΔH_r^o was positive, it was small compared to the positive value of ΔS_r. The negative value of ΔG_r^o also indicated that the reaction to form glycerol monostearate could take place spontaneously under standard conditions and the synthesis could be accelerated using a catalyst.

The obtained heat capacities of all substances were ΔA= 339.73, ΔB= 81.09, ΔC= -32.324 and ΔD= -0.121.

Integral equations (5) and (6) were calculated using MATLAB at 433.15 K, 453.15 K and 473.15 K to obtain the results in Table 3.

Table 1. Molar enthalpy and standard mole entropy under standard conditions

Component	ΔH_f^o (kJ/mol)	ΔS^o (J/mol.T)
$C_3H_8O_3$	-839.16	257.65
$C_{18}H_{36}O_2$	-668.52	204.47
$C_{21}H_{42}O_4$	-1298.82	493.27
H2O	-241.83	188.84

Note: Data were retrieved from (10) and (11)

Table 2. Heat capacities of all reaction substances

Component	A	B	C	D
$C_3H_8O_3$	132.145	0.8600	-0.001974	0.0000018068
$C_{18}H_{36}O_2$	99.012	3.5874	-0.007248	0.0000059035
$C_{21}H_{42}O_4$	686.835	-0.8481	0.0018437	0
H_2O	3.47	1.45	0	0.121

Note: Data were retrieved from (10), (11) and (12)

Table 3. Calculation of integration functions by MATLAB

Temperature	IDCPH	IDCPS
433.15	-5.72E+04	-3.43E+02
453.15	-6.13E+04	-4.04E+02
473.15	-6.45E+04	-4.68E+02

The results of IDCPH and IDCPS were then substituted into equation (4).

Molar enthalpies of formation (H_f) and standard molar entropies (S_m) under standard conditions for glycerol and stearic acid reactions were listed in Table 1. From equations (1), (2) and (3), we obtained a negative ΔG_r^o value (-1.334 kJ/mol). This indicated the reaction to form glycerol monostearate from glycerol and stearic acid was thermodynamically favourable under standard conditions. The reaction was endothermic as the value of ΔH_r^o (45.69 kJ/mol) was positive.

Heat capacities (Cp) of the substances in this reaction are listed in Table 2. These heat capacities were used to obtain Δ values for all substances (ΔA=339.73, ΔB= 81.09, ΔC=-32.324, ΔD= -0.121).

It can be seen from Figure 1 that the reaction of glycerol with stearic acid to form GMS was considerably high, ranging from 0.3561 to 4.362 as the temperature increased from 433.15 K to 473.15 K. In a previous study [16] for the formation of glycerol monostearate from glycerol carbonate and stearic acid under standard conditions, the value of K remained small. On the other hand, K was found to be excessively high, ranging from 6.51 × 10^5 to 13.6 × 10^5, as the temperature was increased from 383.15 K to 413.15 K. Moreover, increasing the reaction temperature can decrease the viscosity and increase the mass transfer of reactants[13]. Commensurate with the Arrhenius equation, when the reaction temperature is increased, the size of the reaction rate constant (k) is more significant. The reaction is faster, and the reaction conversion is higher [20]. This finding indicates that the formation of GMS is both plausible and feasible, while high temperatures are favourable for this reaction.

Table 4. ln K at various temperatures

Temperature	K’	K	ln K (y)
433.15	1.347564	5.76 x10^{24}	57.0132
453.15	1.329933	1.43 x10^{27}	62.5274
473.15	1.313996	2.23 x10^{29}	67.5752

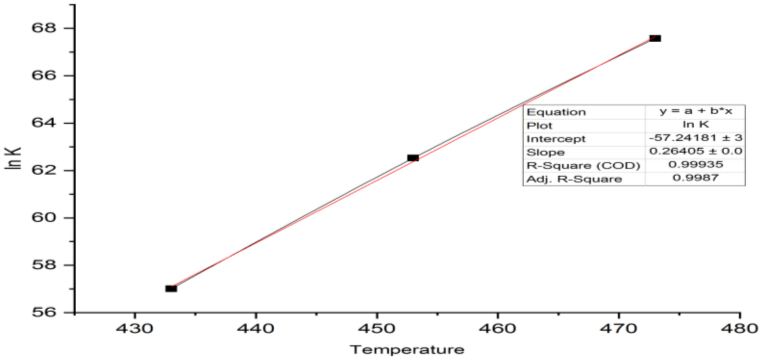

Figure 1. Temperature Vs ln K

Table 6. Reaction components and quantities for yield analysis

No.	Component	ΔG_f^o (kJ/mol)	Mol (initial feed)	Initial guess (mol)**
1	$C_3H_8O_3$	-915.98	1	1.0100
2	$C_{18}H_{36}O_2$	-729.48	1	0.2028
3	$C_{21}H_{42}O_4$	-144.89	0	-0.0020
4	H_2O	262.35	0	-0.0040

** Based on MATLAB; total pressure 1 atm, temperature 298 K

Table 7. The number of C, O and H atoms

	Atom k		
	Carbon(C)	Oxygen (O)	Hydrogen (H)
	A_k= number of atomic mass k in the system		
Component *i*	a_{ik} = number of atom *k* per molecule i		
$C_3H_8O_3$	a $C_3H_8O_{3.}$C= 3	a $C_3H_8O_{3.}$ O= 3	a $C_3H_8O_{3.}$ H= 8
$C_{18}H_{36}O_2$	a $C_{18}H_{36}O_{2.}$C= 18	a $C_{18}H_{36}O_{2.}$ O=2	a $C_{18}H_{36}O_{2.}$H= 36
$C_{21}H_{42}O_4$	a $C_{21}H_{42}O_{4.}$C= 21	a $C_6H_{12}O_6$. O=4	a $C_6H_{12}O_6$.H= 42
H_2O	a $H_2O_.$C= 0	a $H_2O_.$ O= 0	a $H_2O_{.H}$= 2

The atomic mass value k (A_k) can be determined from the initial mole numbers, and the number of atoms k per molecule i(a_{ik})were obtained directly from the chemical formulas of each species as shown in Table 7.

Based on computational analysis, the largest composition of the substances involved in the reaction was found at 473 K with $C_3H_8O_3$ (0.2286 mol), $C_{18}H_{36}O_2$ (0.0620 mol), $C_{21}H_{42}O_4$ (0.4379 mol) and H_2O (0.27131 mol).

Prediction of product yield in this study can be taken into consideration to increase the amount of glycerol monostearate produced from the conversion of glycerol and stearic acid. The results of the prediction of the synthesis without a catalyst are expected to be used as a comparison of data when synthesizing using a catalyst. The catalyst is expected to direct the reaction products so that the main product has a relatively high yield.

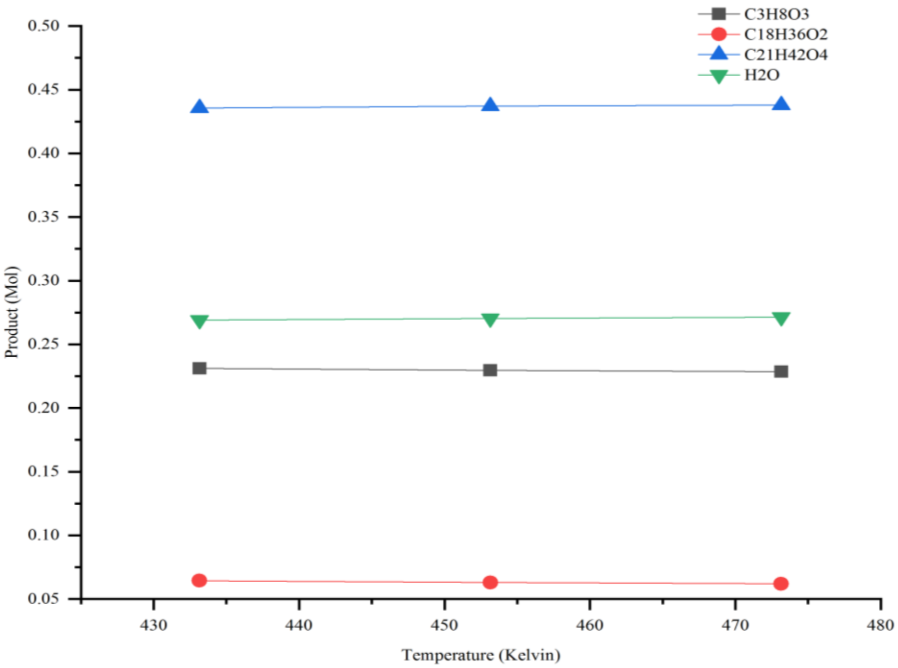

Figure 2. Product yield as a function of temperature

CONCLUSION

The chemical equilibrium constant was determined for the reaction generating GMS from glycerol. The values of ΔH_r^o; ΔS_r^o and ΔG_r^o obtained were +45.69 kJ/mol; +1.144 kJ/mol.K and -1.074 kJ/mol. Glycerolysis of glycerol with stearic acid by esterification was found to be thermodynamically favourable. With a negative ΔG_r^o value (-1.074 kJ/mol), the reaction to produce glycerol monostearate from glycerol would proceed spontaneously and be exothermic under standard conditions. Analysis of the equilibrium constant for this conversion showed a large ln K value (> 1). The prediction used a quadratic equation for equilibrium to determine the unknown variables, and found that increasing the quantity of the reactant increased the product yield at equilibrium. Increasing the temperature was also found to enhance the chemical equilibrium constant for this reaction.

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