

Thermodynamic and Chemical Equilibrium in the Carbonylation the Glycerol with Carbon Dioxide to Produce Glycerol Carbonate by Using Metal Oxide Nanoparticles as Catalyst

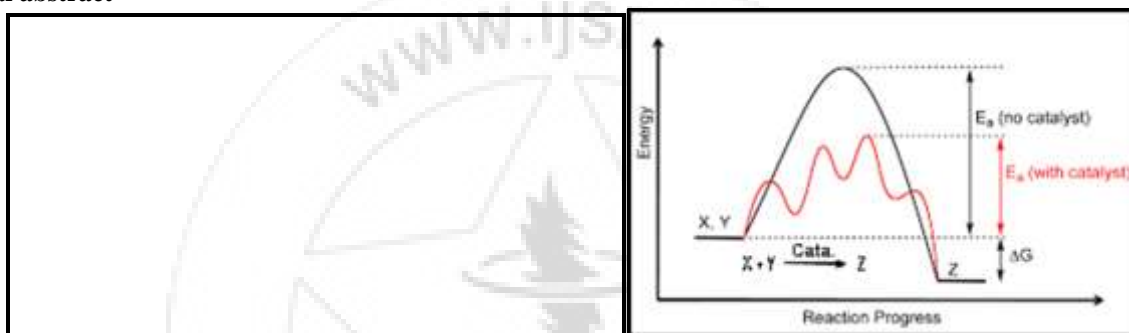
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Graphical abstract



Highlights

- 1) The reaction of glycerol with carbon dioxide is thermodynamically limited.
- 2) The chemical equilibrium constant is still very small even at pressure as high as 5 MPa.
- 3) For the reaction of glycerol with carbon dioxide, the chemical equilibrium constant decreased lightly with the increase of reaction temperature.

Abstract: In this our paper, the Thermodynamic and chemical equilibrium for the glycerol carbonate synthesis from glycerol carbonylation was investigated. The chemical equilibrium constants were calculated for the reactions to produce glycerol carbonate from glycerol. The reaction of glycerol with carbon dioxide is thermodynamically limited. For the reaction of glycerol with carbon dioxide, increasing pressure is favorable to the chemical reaction equilibrium. However, the chemical reaction equilibrium constant is still very small even at pressure as high as 5 MPa. Combined with the effect of temperature on the equilibrium constant described as above, it can be concluded that the reaction of glycerol with carbon dioxide is truly limited in thermodynamics. For the reaction of glycerol with carbon dioxide, the chemical reaction equilibrium constant decreased lightly with the increase of reaction temperature. It can be concluded that the reaction of glycerol with carbon dioxide is thermodynamically unfavorable because the chemical reaction equilibrium constant is quite small. Usually, the yield of glycerol carbonate was small when the reaction of glycerol with carbon dioxide was adopted to produce glycerol carbonate. Thermodynamic data for the reactions for carbonylation of G with CO₂ to GC synthesis at (standard condition), T = 298.15 °K and 101,325 Pa ($\Delta_r H_m^\circ$, $\Delta_r G_m^\circ$, $\Delta_r S_m^\circ$ and K^θ) of the reactions for GC synthesis were (-9.13, -110.85, 23.92 and 6.41×10^{-5}) respectively. That means the reactions for carbonylation of G with CO₂ to GC synthesis was exothermic reaction, quite small chemical reaction equilibrium, spontaneous in the opposite direction. The enthalpy (Heat of reaction) change ($\Delta H_T = 74.946 \text{ kJ} \cdot \text{mol}^{-1}$) is independent of bath and it was endothermic reaction because of the effect of dehydrating agents.

Keywords: glycerol; glycerol carbonate; carbon dioxide; metal oxidenanoparticles catalyst; nanoparticle catalyst; carbonylation; Thermodynamic; Chemical equilibrium.

1. Introduction

Chemical engineering thermodynamics is the study of the interrelation of heat and work with mass transfer in chemical reactions or physical changes of state within the confines of the laws of thermodynamics. Chemical engineering thermodynamics involves not only laboratory measurements

of various thermodynamic properties, but also the mechanism and application of mathematical methods to the study of chemical questions and the spontaneity of processes.

The structure of chemical engineering thermodynamics is based on the first two laws of thermodynamics. Starting from the first and second laws of thermodynamics, four

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equations called the "fundamental equations of Gibbs" can be derived. From these four equations, a multitude of equations, relating the thermodynamic materials properties of the thermodynamic system can be derived using relatively simple mathematics models. The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy (U), enthalpy (H), entropy (S), Helmholtz energy (A), and Gibbs energy (G) in terms of their natural variables. This outlines the mathematical framework of chemical engineering thermodynamics. The term "natural variable" was simply denotes a variable that is one of the convenient variables to describe (U), (H), (G), and (A). When considered as a whole, the four fundamental equations demonstrate but these four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state to a thermodynamic system, and using the fundamental equations, experimental data can be used to determine sought-after quantities like (G) or (H)[1].

In recent years, huge amounts of glycerol (GL) are produced as a by-product of the biodiesel manufactures [2, 3]. Because of rapidly increasing production of global biodiesel in a great quantity, it becomes a research and study focus to transform GL to value-added chemicals. One of the derivatives of GL is the glycerol carbonate (GC), GC has a number of science and industrials applications such as a polar high boiling solvent, chemical intermediate, a surfactant component, carrier in batteries, lubricating oils, monomer for polymers and as components for gas separation membranes [4-6].

GC can be synthesized from GL via several routes, which can be divided into two categories: indirect and direct routes, according to different carbonyl sources. GC can be indirectly synthesized by the transesterification of GL with other organic carbonates and urea. However, carbonates such as dimethyl or diethyl carbonate would be relatively expensive chemicals leading to less commercial benefit for the transesterification of GL with them [7-9]. Meanwhile, ammonia is produced in glycerolizes of urea, which need low-pressure reaction condition to remove the ammonia gas [10-13]. Compared with the indirect route, the direct synthesis of GC by GL carbonylation with CO₂ is more interesting and its atom utilization is as high as 87% [14,

15]. Moreover, this reaction is regarded as a green process in which two cheap raw reactants, GL, a by-product of biodiesel production, and CO₂, a primary greenhouse gas, can be converted to a value-added chemical, Among this method, the most suitable industrial process for producing GC is the carbonylation of GL with CO₂ due to the non-toxic raw material, mild operation condition, high selectivity of GC and simple purification of GC [16-18].

Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy to chemical reaction. Consequently, more molecular collisions have this energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be slowed or blocked by a kinetic barrier. The catalyst can increase reaction rate or selectivity, or enable the reaction at lower conditions (temperatures, pressure). This effect can be illustrated with an energy profile diagram fig.1.

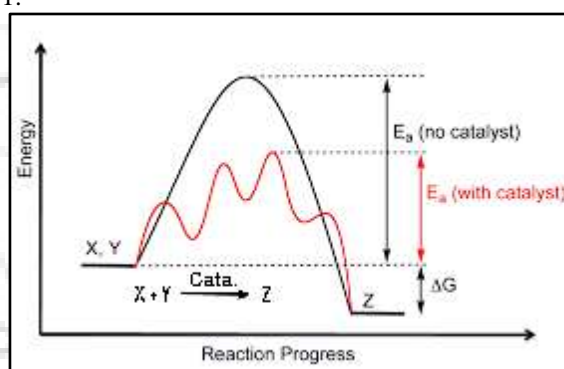


Figure 1: Energy profile diagram

Introducing the catalyst to the system would result in a chemical reaction to move to the new equilibrium side, producing energy. Production of energy is a necessary result since the chemical reactions are spontaneous only if Gibbs free energy was produced, and if there is no energy barrier, there is no need for a catalyst in chemical reaction. Thus, a catalyst that could change the equilibrium and it was contradiction to the laws of thermodynamics [19].

Fig.2 shows the calculations roadmap of primary concern in chemical engineering thermodynamics and chemical equilibrium constant of all cases.

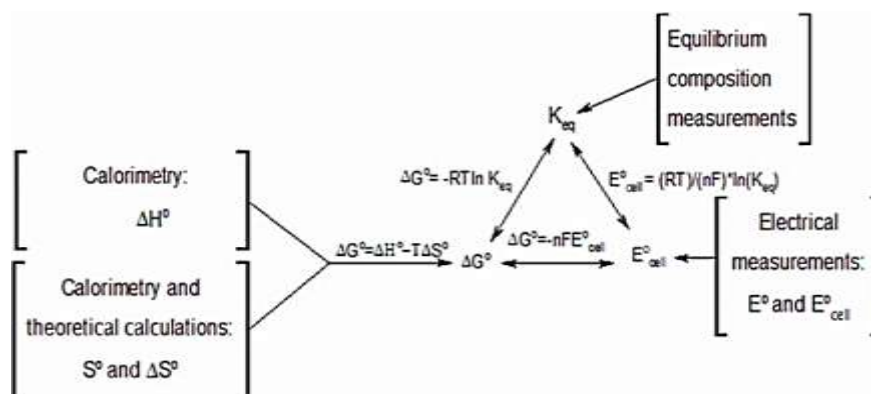


Figure 2: The calculations roadmap of primary concern in chemical engineering thermodynamics and chemical equilibrium constant

2. Methodology of work

2.1. Chemical equilibrium constants for carbonylation reaction of glycerol to produce glycerol carbonate at the standard conditions (T = 298.15 K and 101,325 Pa).

Scheme.1 carbonylation of GL and CO₂ reaction over nanoparticles metal oxide catalysts

The chemical equilibrium constants of the reaction at standard conditions (STP) (T = 298.15 K and 101,325 Pa) can be calculated as follows. The change of standard molar enthalpy $\Delta_r H_m^\theta$ and the change of standard molar entropy $\Delta_r S_m^\theta$ of the chemical reaction can firstly be calculated using equations (1) and (2), if the standard molar enthalpy of formation $\Delta_f H_m^\theta$ and standard molar entropy S_m^θ of all reactants and products in the corresponding phase involved in the chemical reaction can be obtained. Then, $\Delta_r G_m^\theta$ and K^θ for each chemical reaction can be calculated from $\Delta_r H_m^\theta$ and $\Delta_r S_m^\theta$ using equations (3) and (4), the thermodynamic properties such as standard molar enthalpy of formation and standard entropy of the reactants and products in the corresponding phases involved in the above reactions, can be obtained from the handbook [23]. For dimethyl carbonate, glycerol carbonate, and ethylene carbonate, only the gas phase standard molar enthalpy of formation $\Delta_f H_{m,g}^\theta$ and standard molar enthalpy of vaporization $\Delta_v H_{m,g}^\theta$ had been reported [24–27]. So, the liquid standard molar enthalpy of formation $\Delta_f H_{m,l}^\theta$ can be calculated from $\Delta_f H_{m,g}^\theta$ and $\Delta_v H_{m,g}^\theta$ according to equation (5).

$$\Delta_r H_m^\theta = \sum_{\text{Product}} n_i \Delta_f H_{mi}^\theta - \sum_{\text{Reactant}} n_j \Delta_f H_{mj}^\theta \quad (1)$$

$$\Delta_r S_m^\theta = \sum_{\text{Product}} n_i S_{mi}^\theta - \sum_{\text{Reactant}} n_j S_{mj}^\theta \quad (2)$$

$$\Delta_r G_m^\theta = \Delta_r H_m^\theta - T \frac{\Delta_r S_m^\theta}{100} \quad (3)$$

$$\ln K^\theta = 1 + \frac{-\Delta_r G_m^\theta}{RT} \quad (4)$$

$$\Delta_f H_{m,l}^\theta = \Delta_f H_{m,g}^\theta - \Delta_v H_{m,g}^\theta \quad (5)$$

Usually, the liquid standard molar entropy $S_{m,l}^\theta$ of the substances could be calculated from the gas phase standard molar entropy $S_{m,g}^\theta$ and $\Delta_v H_{m,g}^\theta$, of the same substances according to equation (6):

$$S_{m,l}^\theta = S_{m,g}^\theta - \frac{\Delta_v H_{m,g}^\theta}{T} \times 1000 \quad (6)$$

$S_{m,g}^\theta$ Of glycerol carbonate has not been reported. The functional group method by Benson [28] can be used to estimate $S_{m,g}^\theta$ of the substances (equation (7))

$$S_{m,g}^\theta = \sum n_i S_i^\theta - R \ln \delta + R \ln \eta + S_{\text{correction}}^\theta \quad (7)$$

Glycerol carbonate (GC) can be prepared from Carbonation of glycerol (GL) with carbon dioxide (CO₂) (scheme.1) is another method for the production of glycerol carbonate [20–22]. GL was reacted with CO₂ at T = 150 °C and (4–8.2) MPa for 5 h catalyzed by nanoparticles metal oxide, the reaction reaches to the equilibrium state, although the yield of glycerol carbonate is only 39% of glycerol carbonate was obtained from glycerol and carbon dioxide Scheme.1.

n_i is the number of functional group i ; S_i^θ is the additively value of group i ; R is the mole gas constant; $\delta = \delta_{in} \delta_{ext}$, the symmetry number of molecular; δ_{in} is the internal symmetry number of molecular; δ_{ext} is the external symmetry number of molecular; η is the number of enantiomer; $S_{\text{correction}}^\theta$ is the cyclic correction data.

A molecule of substance can be divided into several functional groups according to the structure. Every functional group i has contributed value S_i^θ to $S_{m,g}^\theta$ of the molecule. δ and η are the correction parameters for $S_{m,g}^\theta$ of the molecule based on molecular symmetry and the enantiomer. The $S_{\text{correction}}^\theta$ is the cyclic correction factor for $S_{m,g}^\theta$ of the molecule if it is a cyclic compound.

Because glycerol carbonate is cyclic compound, the cyclic correction factor of the cyclic compound was needed to modify the summation of the group additively in the functional group method of Benson. Then, the values of $S_{m,g}^\theta$ and $S_{m,l}^\theta$ of glycerol carbonate were calculated according to equations (6) and (7).

Based on the functional group and the group additively values [28] in the Benson method for glycerol carbonate as listed in table 1.

Table 1: The functional group and the group additively values for GC

GC	Number of group	S_i^θ (kJ.mol ⁻¹ .k ⁻¹)
C-(H) ₂ (O)(C)	2	41.03
O-(C)(CO)	2	35.31
CO-(O) ₂	1	61.84
C-(C) ₂ (H)(O)	1	- 46.05
O-(H)(C)	1	121.63

For GC, the symmetry number of molecular $\delta = 1$, the number of enantiomer $\eta = 2$. The group additively values are from the literature [28].

2.1.1 The effect of temperature on the chemical equilibrium constants.

The values of the liquid heat capacity $C_{p,m,l}$ of GC was estimated by using the Rozička-Domalski functional group method [29], which is a method normally used to estimate the liquid heat capacity according to the molecular structure.

The heat capacity for other substances in a different phase could also be obtained from the literature. [29]

The change of molar heat capacity of reaction $\Delta_r C_{p,m}$ can be calculated (equation (8)). Here, it is assumed that $\Delta_r C_{p,m}$ and $\Delta_r H_m$ are independent of the pressure (constant pressure). Then, the change of molar enthalpy for each reaction $\Delta_r H_m$ at different temperatures can be calculated based on equation (9). The value of $\Delta_r G_m(298.15\text{K}, P)$ can be obtained by Eq. (14). Based on equation (10) and $\Delta_r G_m(298.15\text{K}, P)$, the change of Gibbs free energy of reaction $\Delta_r G_m(T, P)$ and the effect of temperature on the thermodynamic equilibrium constant K can be obtained.

$$\Delta_r C_{p,m} = \sum_{\text{Product}} \Delta_r C_{p,m,i} - \sum_{\text{Reactant}} \Delta_r C_{p,m,j} \quad (8)$$

$$\left[\frac{\delta \Delta_r H_m}{\delta T} \right]_P = \Delta_r C_{p,m} \quad (9)$$

$$\left[\frac{\delta \Delta_r G_m / T}{\delta T} \right]_P = -\Delta_r H_m / T^2 \quad (10)$$

$$\left(\frac{\partial \Delta_r G_m}{\partial P} \right)_T = \Delta n RT \quad (11)$$

By integration, equation (11) becomes equation (12).

$$\Delta_r G_m(T, P) = -RT \ln K \quad (12)$$

The value of $\Delta_r G_m(T, P)$ can be calculated according to equations (8)-(10). Then, the chemical equilibrium constants at different pressure can be calculated according to equation (12).

2.1.2 The effect of pressure on the chemical equilibrium constants.

For the reaction involving gas CO_2 , pressure also has an influence on the thermodynamic equilibrium (K). When the reaction temperature (T) is constant,

$$\Delta n = \sum_{\text{Product}} \nu_{i(g)} - \sum_{\text{Reactant}} \nu_{j(g)} \quad (13)$$

$\nu_{i(g)}$, $\nu_{j(g)}$ are stoichiometric coefficient of gas substance.

By simple integration, equation (12) becomes equation (14). The value of $\Delta_r G_m(T, P^\theta)$ can be calculated according to equations (8)-(10).

$$\Delta_r G_m(T, P) = \Delta_r G_m(T, P^\theta) + \Delta n RT \ln \left(\frac{P}{P^\theta} \right) \quad (14)$$

For reaction of glycerol with carbon dioxide, Δn is not 0, so the reaction pressure can influence the $\Delta_r G_m(T, P)$ and on the corresponding chemical equilibrium.

2.2. Thermodynamic of dehydration reaction.

In chemistry and the biological sciences, a dehydration reaction, also known as Zimmer's Hydrogenesis, is a chemical reaction that involves the loss of a water molecule from the reacting molecule. Dehydration reactions are a subset of condensation reactions. Because the hydroxyl group (-OH) is a poor leaving group, having a Bronsted acid catalyst often helps by protonating the hydroxyl group to give the better leaving group (-OH₂⁺). The reverse of a dehydration reaction is a hydration reaction. Common dehydrating agents used in organic synthesis include concentrated sulfuric acid, concentrated phosphoric acid, hot aluminum oxide and hot ceramic.

A homogeneous dehydrating is used, and then an additional separation step to separate the dehydrating agent is needed. This stream will consist of reacted agent and unreacted agent and needs to be regenerated to obtain a pure stream of dehydrating agent again. Two designs are developed for this. One with a recycle to the regeneration reactor and one without a recycle, this will depend on the conversion of the reactor. A last option is to recover the dehydrating agent as quickly as possible. In this way the loss of dehydrating agent can be minimized [30].

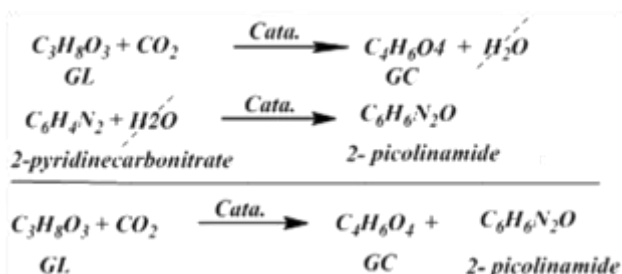
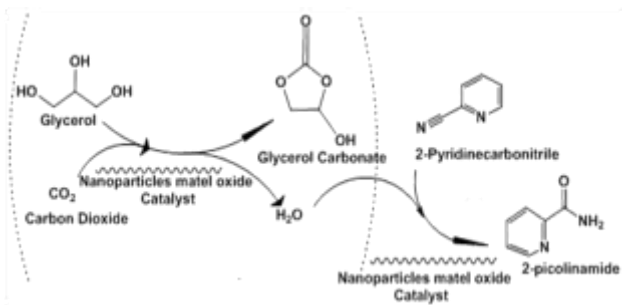
To select a good dehydrating agent, a list of requirements for the agent was set up. Obviously, the goal of the agent is to remove water, and therefore the compound should react with water. It should be powerful enough to do this. Thus, it should already react with water when there is only a very small amount of water. In addition, it should do this sufficiently fast enough. What hereafter is important? is the ability to do this at favorable operating conditions.

Another key aspect of the agent is its recoverability or it should very cheap so that one time use is still economically feasible. In addition, there are requirements that not necessary have to be fulfilled but can result in problems. To summarize, the requirements are listed below with bullet points.

- React with water (chemical or physical)
- Reaction with water significantly powerful
- Reaction with water significantly fast
- Able to react within operating window
- Recoverable, or very cheap
- No or negligible side reactions
- Available at significant quantities
- Not corrosive

Various dehydrating agents examined against the list of requirements. 2-Cyanopyridine is a promising dehydrating agent for this process, as is stated before in this report. Actually, the article of Bansode et al. was the motive for this research [31]. However, the problem with this agent is that little knowledge is available about the recoverability of 2-cyanopyridine. It was reported by Honda et al. that it is possible to recover 2-picolinamide back to 2-cyanopyridine [32]. However, the time needed for 90% conversion is about 500h.

The process of glycerol carbonate formation by the intermolecular rearrangement of the A species is the rate-determining step. Glycerol carbonate was obtained from the carbonylation of glycerol and CO_2 over metal oxide nanoparticles catalysts with the dehydrating agent of 2-pyridinecarbonitrile as the coupling reaction. As shown in Scheme.2, in the catalyst/2-pyridinecarbonitrile system, glycerol reacts with CO_2 over catalyst surface to produced glycerol carbonate and H_2O , while the formed H_2O reacts with dehydrating agent 2-pyridinecarbonitrile (2-cyanopyridine) to produced (2-picolinamide) and removed H_2O from the reaction system to pull water from the middle of the chemical reaction as side product and shift the chemical equilibrium to the GC production side and the chemical reaction bath doesn't return back to reverse direction to produce GL as (scheme.2 and fig.3)[33].



Scheme.2 Carboxylation of GL and CO₂ reaction over nanoparticles metal oxide catalysts with dehydrating reaction.

calculated to be 525.56 J. °K⁻¹.mol⁻¹ according to equation (7). It was reported that $\Delta_r H_m^\theta$ of glycerol carbonate was 85.9 J.mol⁻¹ [24]. So, the S_m^θ of glycerol carbonate was determined to be 237.45J.K⁻¹.mol⁻¹ according to equation (6). The standard molar enthalpies of formation and standard molar entropies of the substances involved in reactions for glycerol carbonate synthesis are listed in table.2. [24]

Table 2: Standard molar enthalpy of formation and standard mole entropy of all substances involved in reactions for GC synthesis, **scheme.1**

substances	Phase	$\Delta_f H_m^\theta$ (kJ.mol ⁻¹)	S_m^θ (kJ.mol ⁻¹)
GL	Liquid	- 668.52	204.47
CO ₂	Gas	- 393.50	213.78
GC	Liquid	- 785.32g	237.45i
H ₂ O	Liquid	- 285.83	69.950

According to the standard molar enthalpies of formation and standard molar entropies listed in table 3, $\Delta_r H_m^\theta$ and $\Delta_r S_m^\theta$ of the reactions for GC synthesis can be obtained. Then, $\Delta_r G_m^\theta$ and K^θ for each reaction can be calculated from $\Delta_r H_m^\theta$ and $\Delta_r S_m^\theta$. The results are listed in table 3. The standard chemical equilibrium constant for the reaction of glycerol with carbon dioxide was quite small at the standard conditions.

Table 3: Thermodynamic data for the reactions for carbonylation of G with CO₂ to GC synthesis at (standard condition), T = 298.15 °K and 101,325 Pa.

Reaction	$\Delta_r H_m^\theta$ (kJ.mol ⁻¹)	$\Delta_r S_m^\theta$ (kJ.mol ⁻¹)	$\Delta_r G_m^\theta$ (kJ.mol ⁻¹)	K^θ
GL + CO ₂ (Scheme.1)	- 9.13	- 110.85	23.92	6.41×10 ⁻⁵

Figure 3: Enthalpy profile diagram.

$$\Delta H_p^\theta = \left(\sum n_i C_{p_{min}}^\theta \right) (T_2 - 298.15) \quad (15)$$

$$\Delta H_T = \Delta_r H_m^\theta + \Delta H_p^\theta \quad (16)$$

3. Results and discussion

3.1 Calculation of the $\Delta_r H_m^\theta$, $\Delta_r S_m^\theta$, $\Delta_r G_m^\theta$ and K^θ .

According to the standard molar enthalpies of formation and standard molar entropies listed in table.2, the data of G, CO₂ and H₂O were retrieved in the handbook [23] and the $\Delta_f H_m^\theta$ of GC was obtained from equation (5) and the literature [24–27] and S_m^θ of GC was calculated using the Benson functional group method (equation (7)) and used table.1.

Based on the functional group and the group additively values [28] in the Benson method for ethylene carbonate as listed in table 4, the ($S_{correction}^\theta$) of glycerol carbonate was determined to be 229.69 J. °K⁻¹.mol⁻¹ according to equation (7). Combined with the functional group and group additively values [28] in the Benson method for glycerol carbonate as listed in table 5, and ($S_{correction}^\theta$) of cyclic alkylene carbonate, the S_{mg}^θ of glycerol carbonate was

3.2 The effect of temperature on the chemical equilibrium constants.

In order to calculate chemical equilibrium constants at different temperatures, liquid heat capacity $C_{p,m,l}$ of glycerol carbonate (GC) was estimated by the functional group method of Rozicka-Domalski and heat capacity values for other substances (GL, CO₂, H₂O) in a different phase were obtained from the handbook [29]. The data of the heat capacity are listed in table 4. The effect of temperature on the chemical equilibrium constant was determined, as described in section 2.3 using equations (8)-(10), (and) (12), and the results are shown in table 5.

For the reaction of glycerol (GL) with carbon dioxide (CO₂), the chemical equilibrium constant also decreased slightly with the increase of reaction temperature. It can be concluded that the reaction of glycerol with carbon dioxide is thermodynamically unfavorable because the chemical equilibrium constant is quite small. Usually, the yield of glycerol carbonate was small when the reaction of glycerol with carbon dioxide was adopted to produce glycerol carbonate [20, 21].

Table 4: Heat capacity of the reactions substances for carbonylation of G with CO₂ to GC synthesis.

$$C_{p,m,i}(J.^{\circ}K^{-1}.mol^{-1}) = a + bT + cT^2 + dT^3 + eT^4$$

substances	Phase	A	b×10 ²	c×10 ⁴	d×10 ⁶	e×10 ¹⁰
GL	Liquid	132.145	86.007	-19.745	1.806	0.0
CO ₂	Gas	27.090	1.127	1.248	-1.973	0.878
GC	Liquid	6.970	-99.040	44.700	0.0	0.0
H ₂ O	Liquid	92.053	-3.995	-2.110	0.534	0.0

* C_{p,m,i} is the mole isobaric heat capacity a, b, c, d, e are coefficients in the equation of C_{p,m,i}.

Table 5: Chemical equilibrium constants (K) at different temperatures

T (°K)	T (°C)	K GL+CO ₂ Reaction (Scheme.1)
298.15	25	3.27 × 10 ⁻³
313.15	40	2.723 × 10 ⁻³
333.15	60	2.161 × 10 ⁻³
353.15	80	1.769 × 10 ⁻³
373.15	100	1.513 × 10 ⁻³
393.15	120	1.366 × 10 ⁻³
413.15	140	1.314 × 10 ⁻³
433.15	160	1.355 × 10 ⁻³
453.15	180	1.506 × 10 ⁻³

3.3. The effect of pressure on the chemical equilibrium constants (K).

For the reaction of GL with CO₂, Δn were not zero, so the reaction pressure can influence Δ_rG_m(T, P) and the corresponding chemical equilibrium. The effect of reaction pressure on the K for the reaction of GL with carbon dioxide was determined using equations (8)–(10), (14), and (15) (described in section 2), and the results are shown in table 6.

For the reaction of glycerol with CO₂, increasing pressure is favorable to the chemical equilibrium. However, the K is still very small even at pressure as high as 5 MPa. Combined with the effect of temperature on the K described as above, it can be concluded that the reaction of glycerol with carbon dioxide is truly limited in thermodynamics. For the reaction of glycerol with urea, decreasing the pressure is favorable to yield glycerol carbonate.

Table 6: Effect of reaction pressure on K for the reaction of GL with CO₂

P (Pa)	^a . P/P ⁰	^b . K GL+CO ₂ Reaction (Scheme.1)
0.01996	0.000197	2.19 × 10 ⁻⁹
0.1013	0.001	1.11 × 10 ⁻⁸
1.013	0.01	1.11 × 10 ⁻⁷
10.13	0.1	1.11 × 10 ⁻⁶
101.3	1.0	1.11 × 10 ⁻⁵
1013.25	10	1.11 × 10 ⁻⁴
2026.5	20	2.22 × 10 ⁻⁴
3039.75	30	3.33 × 10 ⁻⁴
4053.0	40	4.44 × 10 ⁻⁴
5066.25	50	5.55 × 10 ⁻⁴

^a. at P/P⁰ is the ratio of reaction pressure to the standard pressure 101,325 Pa.

^b. at (T = 453.15 °K = 180 °C).

3.4 The effect of dehydrating agents on the heat of reaction (ΔH_T)

Estimated the mean specific heat (C_{p,m,i}) of (CO₂, H₂O, 2-cyanopyridine and 2-picolinamide) for GC synthesis, scheme.2 by using fig.(4,5,6, and 7) the data of the mean heat capacity are listed in table 7. The total of Standard molar enthalpy of formation (Δ_fH⁰_m) was determined by using scheme.2, and the results are shown in table 7.

Table 7: Standard molar enthalpy of formation(Δ_fH⁰_m) and mean specific heat (C_{p,m,i}) of all substances involved in reactions for GC synthesis, scheme.2 and Fig..2.

substances	Phase	Δ _f H ⁰ _m (kJ.mol ⁻¹)	C _{p,m,i} (J.mol ⁻¹ .°K)	References
GL	Liquid	-668.52	279.374	[20,21,24]
CO ₂	Gas	-393.50	45.667	[34 – 36]
GC	Liquid	-785.32g	388.262	[20,21,24]
H ₂ O	Liquid	-285.83	77.827	[24,36]
C ₆ H ₄ N ₂	Liquid	209.97	141.637	[24,36]
C ₆ H ₆ N ₂ O	Liquid	-156.3	172.742	[24,36]

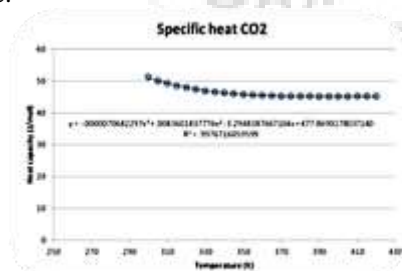


Fig.4 Specific heat of carbon dioxide at 30 bar [36]

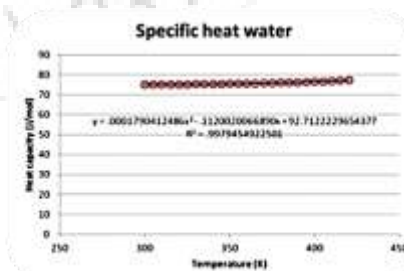


Fig. 5. Specific heat of water at 30 bar [36].

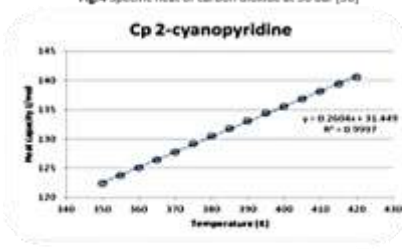


Fig. 6 Specific heat of 2-cyanopyridine at 1 bar [24 and 36]

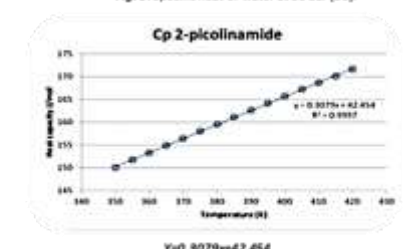


Fig. 7 Specific heat of 2-picolinamide at 1 bar [24 and 36]

$$\text{Heat of reaction } \Delta H_T = \Delta_r H_m^\theta + \Delta H_p^\theta$$
$$\Delta H_T = -9.21043 + 84.156 = 74.946 \text{ kJ.mol}^{-1}$$

This enthalpy (Heat of reaction) change (ΔH_T) is independent of bath and it was endothermic reaction and identical to the cases in ref. [33]

4. Conclusions

Thermodynamic data for the reactions for carbonylation of G with CO₂ to GC synthesis at (standard condition), T = 298.15 °K and 101,325 Pa ($\Delta_r H_m^\theta$, $\Delta_r G_m^\theta$, $\Delta_r S_m^\theta$ and K^θ) of the reactions for GC synthesis were (-9.13, -110.85, 23.92 and 6.41×10^{-5}) respectively. That means the reactions for carbonylation of G with CO₂ to GC synthesis was exothermic reaction, quite small chemical reaction equilibrium, spontaneous in the opposite direction.

The chemical equilibrium constant decreased slightly with the increase of reaction temperature. It can be concluded that the reaction of glycerol with carbon dioxide is thermodynamically unfavorable because the chemical equilibrium constant is quite small. Usually, the yield of glycerol carbonate was small when the reaction of glycerol with carbon dioxide was adopted to produce glycerol carbonate.

For the reaction of glycerol with carbon dioxide, increasing pressure is favorable to the chemical equilibrium. However, the chemical equilibrium constant is still very small even at pressure as high as 5 MPa. Combined with the effect of temperature on the equilibrium constant described as above, it can be concluded that the reaction of glycerol with carbon dioxide is truly limited in thermodynamics.

The enthalpy (Heat of reaction) change ($\Delta H_T = 74.946 \text{ kJ.mol}^{-1}$) is independent of bath and it was endothermic reaction because of the effect of dehydrating agents.

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