Calculation study on acetic acid selective hydrogenation to ethanol for bio-oil upgrading

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Abstract. In this paper, the thermodynamics on the hydrogenation of acetic acid as a typical model compound of bio-oil was simulated based on the principle of Gibbs free energy minimization. The reaction material system was determined according to the reaction mechanism of the selective hydrogenation of acetic acid to ethanol. The influences of reaction conditions on the equilibrium products were mainly studied. The results show that methanation is easy to occur in the hydrogenation system. For the simplified reaction system with a consideration of main reactions, the results showed that lower temperature (370-530 K), higher pressure (3.0-9.0 MPa), higher molar ratio of hydrogen to acetic acid (2.0-6.0) and lower water content are beneficial to increase acetic acid conversion and ethanol selectivity. In addition, the calculated results are compared with the experimental results.

1. Introduction

With the increasing reduction of fossil energy and the increasingly prominent environmental problems, it is very important to develop biomass energy. Biomass pyrolysis oil needs to be converted to improve quality because of its acid content. Acetic acid hydrogenation is an important transformation because acetic acid is a typical model compound of bio-oil. The current price of ethanol is higher than that of acetic acid. Therefore, the hydrogenation of acetic acid to ethanol can not only alleviate the energy crisis, but also realize economic benefits.

Acetic acid hydrogenation is a complex reaction system with a series of products, including ethanol, ethyl acetate, acetaldehyde, methane, ethane and so on. For acetic acid hydrogenation, many studies focus on the research and improvement of the catalyst, but less on the thermodynamics of the related reaction systems. Zhang et al [1] prepared the Pt-Sn bimetallic catalyst for acetic acid hydrogenation. The conversion of acetic acid reached 97% and the selectivity of ethanol reached 92%. Using infrared spectroscopy, microcalorimetry method and kinetic measurement technology, the selective hydrogenation process of acetic acid on Cu/SiO$_2$ catalyst were studied by Natal Santiago et al [2]. The thermodynamic study of acetic acid hydrogenation can be seen in the literature [3, 4], but the number of reaction equations considered in these analyses is less.

In this paper, based on the minimum principle of Gibbs free energy and related reaction mechanism of acetic acid hydrogenation, the thermodynamics of acetic acid hydrogenation to ethanol of main
target product was analyzed by using Aspen plus software. The effects of reaction temperature, pressure and ratio of hydrogen to acetic acid on the equilibrium composition were investigated, which could provide a reference for the experimental process.

2. Calculation Principles and Methods

2.1 Reaction mechanism analysis

According to the related reaction mechanism of the acetic acid hydrogenation [5-7], a typical reaction path network is shown in Figure 1. The reactions included in Figure 1 are summarized in Table 1.

![Figure 1. Pathway of acetic acid hydrogenation [5,6]](image)

Table 1. Reactions in the system of acetic acid hydrogenation

| Reaction Equation                                      | No. |
|--------------------------------------------------------|-----|
| CH$_3$COOH + H$_2$ → CH$_3$CHO + H$_2$O                | (1) |
| CH$_3$CHO + H$_2$ → C$_2$H$_5$OH                       | (2) |
| CH$_3$COOH + C$_2$H$_5$OH → CH$_3$COOC$_2$H$_5$ + H$_2$O | (3) |
| CH$_3$CHO + CH$_3$CHO → CH$_3$COOC$_2$H$_5$            | (4) |
| CH$_3$COOC$_2$H$_5$ + 2H$_2$ → 2C$_2$H$_5$OH           | (5) |
| C$_2$H$_5$OH → C$_2$H$_4$ + H$_2$O                      | (6) |
| C$_2$H$_4$ + H$_2$ → C$_3$H$_6$                        | (7) |
| CH$_3$COOH + H$_2$ → CH$_3$CHO + CO + H$_2$O           | (8) |
| CO + 3H$_2$ → CH$_4$ + H$_2$O                           | (9) |
| 2CH$_3$COOH → CH$_3$COCH$_3$ + CO$_2$ + H$_2$O         | (10)|

In the process of acetic acid hydrogenation, there are hydrogenation of acetic acid to acetaldehyde (1), hydrogenation of acetaldehyde to ethanol (2), esterification (3), tishchenko reaction (4), hydrogenolysis reaction (5), ethanol dehydration reaction (6), ethylene hydrogenation (7), hydrogenation of decarbonylation (8), methanation reaction (9) and ketone reaction (10). In addition, there is a reverse water gas shift (RWGS) reaction (CO$_2$ + H$_2$ → CO + H$_2$O).

According to the pathway of acetic acid hydrogenation, the main reactions are as follows: acetic acid hydrogenation to acetaldehyde (1), hydrogenation of acetaldehyde to ethanol (2) and esterification of acetic acid with ethanol (3). In addition, there are some side reactions (4-11). The overall reaction of reaction (1) and (2) is CH$_3$COOH + 2H$_2$ → CH$_3$CHOH + 2H$_2$O.
2.2 Thermodynamic data
According to the thermodynamic data of the substances involved in the reaction, the reaction heat and equilibrium constant at different temperatures were calculated. In the hydrogenation of acetic acid, enthalpy change ($\Delta H_f$), Gibbs free energy change ($\Delta G_f$) and equilibrium constant ($K_f$) were calculated using the formula (1) - (4) respectively.

$$\Delta H_f = \sum_j v_j \Delta H_{j298K} + \sum_j \int_{298}^T C_j dT$$

(1)

$$\Delta S_f = \sum_j v_j \Delta S_{j298K} + \sum_j \int_{298}^T v_j C_j dT$$

(2)

$$\Delta G_f = \Delta H_f - T \Delta S_f$$

(3)

$$\ln K_f = - \frac{\Delta G_f}{RT}$$

(4)

2.3 Calculation Method and Parameters
The thermodynamic calculation was carried out by RGibbs Gibbs reactor model in Aspen Plus software. The Gibbs free energy minimization method is widely used to analyze the equilibrium composition of complex reaction system. According to the reaction mechanism, the reaction systems of acetic acid hydrogenation were determined.

Multiple reaction system (denoted by MRS): The main and side reactions (1-10) were considered in the reaction system. The selected substances in the reaction system are CH$_3$COOH (HAC), H$_2$, C$_2$H$_5$OH (EtOH), CH$_3$CHO (AH), CH$_3$COOC$_2$H$_5$ (EAC), CH$_4$, C$_2$H$_4$, C$_2$H$_6$, CO$_2$, CO and H$_2$O.

Simplified reaction system (denoted by SRS): The main reactions (1-3) were only considered in the reaction system. The substances in the reaction system are CH$_3$COOH (HAC), H$_2$, C$_2$H$_5$OH(EtOH), CH$_3$CHO(AH), CH$_3$COOC$_2$H$_5$(EAC) and H$_2$O. Other substances are not considered.

In the thermodynamic analysis, the Peng-Robinson equation of state was selected because of the existence of non ideal gas in the system. The effects of reaction conditions on the conversion rate of raw materials and the selectivity of the products were mainly discussed. The conversion rate of raw materials and the selectivity of the product are defined as follows, respectively.

**Conversion rate of acetic acid:**

$$X(\text{HAC}) = \left( \frac{F_{\text{HAC, out}} - F_{\text{HAC, in}}}{F_{\text{HAC, in}}} \right) \times 100\%$$

(5)

**Selectivity of the product:**

$$S(i_c) = \left[ \lambda \frac{F_{i_c, out}}{F_{i_c, in}} \right] \times 100\%$$

(6)

In which, $X(\text{HAC})$ is the conversion rates of acetic acid, $F_i$ is the molar flow rate of species i and the subscripts of in and out indicate the state of being in and out, respectively. $S(i_c)$ is the selectivity of carbonaceous substances, in which $\lambda$ is the number of carbon atoms in species i.

3. Results and discussion

3.1 Analysis of thermodynamic parameters
In the reaction system of acetic acid hydrogenation, the standard molar reaction enthalpy, Gibbs free energy and equilibrium constant with the change of temperature are shown as shown in Figure 2.
As shown in Figure 2 (a), the molar enthalpy changes of each reaction vary slightly with the change of temperature. The reactions (1, 6, 10) are endothermic reactions, and the reaction (8) is endothermic at low temperature and exothermic reaction at high temperature, and the reactions (2, 3, 4, 5, 7, 9) are exothermic reactions. In the range of reaction temperature, the output of heat of the reactions (2, 3, 7, 9) are greater than 40 kJ/mol, which are strong exothermic reactions.

From Figure 2 (b), it is known that the Gibbs free energy of the reactions (2, 4, 5, 7, 9) increases with the increase of reaction temperature, and the reaction (3) does not change with temperature. The rest reactions (1, 6, 9, 10) decrease with the increase of temperature. At a higher temperature, the Gibbs free energy of the reaction (2, 4, 5) becomes positive, and the reaction can not be carried out spontaneously. The Gibbs free energy of the reaction (1, 6) becomes positive at low temperature. With the increase of temperature, the reaction (1, 6) Gibbs free energy is reduced to negative and the reaction can be carried out spontaneously. The Gibbs free energy of reaction (8, 10) is always less than -20 kJ/mol.

From Figure 2 (c), the equilibrium constants of each reaction are different. The equilibrium constant Kp of methane formation (9) reaches $10^{10}$ at 498 K, while the reaction of producing ethanol (2) in main reaction is only 4.79. The reaction temperature has a great influence on the equilibrium constant of each reaction. The equilibrium constant of ethanol production (2) is $1.86 \times 10^5$ at 298 K, and only $3.26 \times 10^{-3}$ at 898 K, indicating that this reaction is greatly inhibited at high temperature and so it is suitable for low temperature reaction.

3.2 Effects of reaction conditions on the multiple reaction system (MRS)

The thermodynamic analysis on the multiple reaction system of acetic acid hydrogenation was carried out under the conditions of reaction temperature (298-898 K), pressure (0.5-15 MPa) and H2/HAC molar ratio (0.2-15). The influences of reaction conditions on the equilibrium system of MRS are shown in Figure 3.
Figure 3. Effects of reaction conditions on the multiple reaction system (MRS) of acetic acid hydrogenation. Reaction conditions: (a) $H_2$/HAC = 6.0, 3.0 MPa; (b) $H_2$/HAC = 6.0, 498 K; (c) 3.0 MPa, 498 K.

From figure 3, the conversion rate of acetic acid is always close to 100% and CH$_4$ selectivity is near 100%. This is because that methanation reaction (9) is thermodynamically easy to occur. In the system of MRS, except for CH$_4$ and a small amount of CO and CO$_2$, the amounts of other carbon containing products are almost zero. Therefore, in order to analyze the effect of acetic acid hydrogenation on the target product of ethanol, the simplified reaction system (without methanation) was simulated and analyzed.

3.3 Effects of reaction conditions on the simplified reaction system (SRS)

3.3.1 Effects of temperature and pressure. The effects of temperature and pressure on the equilibrium system of SRS were analyzed under the conditions of temperature of 298-718 K, pressure of 1.0-9.0 MPa and $H_2$/HAC molar ratio of 6.0. Figure 4 shows the effects of the temperature and pressure on the equilibrium conversion and product selectivities of SRS.
Figure 4. Effects of temperature and pressure on equilibrium conversion and product selectivities of SRS.

(a) $X_{(HAC)}$; (b) $S_{(EtOH)}$; (c) $S_{(AH)}$; (d) $S_{(EAC)}$. Reaction condition: $H_2/HAC=6.0$

As shown in Figure 4, the conversion rate of acetic acid is higher than 95%. With the increase of reaction temperature and the decrease of pressure, $X_{(HAC)}$ decreases, $S_{(EtOH)}$ decreased gradually, and $S_{(AH)}$ and $S_{(EAC)}$ increase. This is because the overall reaction of acetic acid hydrogenation is exothermic reaction and high temperature is not conducive to the positive reaction. The hydrogenation of acetic acid to ethanol is a reaction of decreasing number of gas molecules, indicating that increasing pressure is beneficial to the hydrogenation reaction. Under the condition of low pressure, $S_{(EAC)}$ increases with the temperature first and then gradually decreased. This is because the formation and hydrogenolysis of ethyl acetate are sensitive to temperature. In a certain temperature range, increasing temperature can make ethanol and acetic acid react to form ethyl acetate. When the temperature is higher, ethyl acetate hydrogenolysis reaction is intensified, resulting in the decrease of ethyl acetate selectivity.

From the above analysis, low temperature and high pressure is beneficial to the hydrogenation reaction. But reaction temperature has an effect on the rate of reaction and high pressure will increase equipment investment, operation cost and safety risk. Therefore, it is necessary to select the operating conditions and to choose a reasonable catalyst.

3.3.2 Effect of Reactant ratio. The effects of the molar ratio of $H_2/HAC$ and $H_2O$ content ($H_2O/HAC$ mole ratio) in the reactants on the reaction equilibrium system were considered. Figure 5 shows the effect of $H_2/HAC$ mole ratio and $H_2O$ content on the equilibrium conversion and product selectivities of SRS.

Figure 5(a) shows that the conversion rate of acetic acid increases with the increase of the ratio of $H_2/HAC$. When $H_2/HAC$ ratio is greater than 2.0, the conversion rate of acetic acid increased to more than 96% and the pressure has no significant effect on the conversion of acetic acid. The selectivity of ethanol increased with the increase of $H_2/HAC$ ratio and the increase of pressure. When the ratio of $H_2/HAC$ is 6.0, $S_{(EtOH)}$ is more than 80%. $H_2/HAC$ increases after 6.0, the selectivity of ethanol has not been significantly improved. The selectivity of acetaldehyde decreased with the increase of pressure and basically unchanged with the change of $H_2/HAC$. The selectivity of acetaldehyde is low, mainly because acetaldehyde is the intermediate product and it is basically converted into ethanol during the reaction process. The selectivity of ethyl acetate decreased with the increase of the ratio of $H_2/HAC$ and the increase of pressure. In the case of $H_2/HAC$ below 3.0, the value of $S_{(EAC)}$ is high. This is mainly because of the esterification (3) and tishchenko reaction (4).

The above analysis shows that the increase of $H_2/HAC$ ratio will improve the conversion rate of acetic acid and the selectivity of ethanol, but the excessive proportion of $H_2/HAC$ will cause the waste of hydrogen and increase the cost of production, therefore the suitable $H_2/HAC$ range is 2.0-6.0.
Figure 5. Effects of H₂/HAC mole ratio and H₂O content on the equilibrium conversion and product selectivities of SRS. (a) Effect of H₂/HAC mole ratio; (b) Effect of H₂O content.

As shown in Figure 5(b), the conversion rate of acetic acid is basically above 99%. The addition of water has no significant effect on the conversion of acetic acid. S(AH) and S(EAC) are also basically unchanged with the increase of water content. S(EtOH) slightly decreases with the increase of water content. When the presence of no water exists, S(EtOH) is 83.6%. While S(EtOH) decreases to 82.0% when the molar ratio of H₂O/HAC is 1.0.

3.4 Results comparison

The thermodynamic calculation is compared with the related research results, as shown in Table 2.

| catalyst / Calculation method | Reaction conditions | X(HAC) | S(EtOH) | References |
|-----------------------------|---------------------|--------|---------|------------|
| Ni-Mo/γ-Al₂O₃               | 453 K, 4.0 MPa      | 81.2 % | 22.0 %  | [8]        |
| Pt-Sn/CaSiO₃-SiO₂           | 598 K, 2.2 MPa, H₂/HAC=15.0 | 90.7 % | 87.0 %  | [9]        |
| Pt-Sn/Al₂O₃                | 548 K, 2.0 MPa      | 64.0 % | 93.0 %  | [10]       |
| Pt-Co/SiO₂                 | 523 K, 2.2 MPa      | 71.0 % | 96.0 %  | [11]       |
| Gibbs free energy minimization | T=373 K, P=10.0 MPa, H₂/HAC=4.0 | >70.8 % | -       | [3]        |
| Gibbs free energy minimization | SRS system: T=538 K, P=3.0 MPa, H₂/HAC=6.0 | 98.7 % | 69.0 %  | This study |

The results of Table 2 show that the conclusions of this study are in accordance with the relevant research conclusions. From the comparison between thermodynamic and experimental results, it can be seen that the conversion rate of raw materials and selectivity of target products are lower than those of thermodynamic optimization. This indicates that the catalyst should be further improved to achieve better performance.

4. Conclusions

In this paper, the thermodynamics on acetic acid hydrogenation system was simulated. The effects of reaction conditions on the equilibrium products were analyzed. The results of the study are in agreement with the experimental results. The main conclusions of this study are as follows:

(1) For the multiple reaction system (MRS) of acetic acid hydrogenation with a comprehensive consideration of main reactions and side reactions, the conversion rate of acetic acid is always close to
100%. There are a large amount of CH$_4$ and a small amount of CO$_2$ and CO in product. The selectivities of other carbon-containing products are very low.

(2) For the simplified reaction system (SRS) of acetic acid with a consideration of the main reactions, the conversion of acetic acid is over 97% when H$_2$/HAC is greater than 2.0. Low temperature, high pressure and high mole ratio of hydrogen to acetic acid are beneficial to the hydrogenation of acetic acid to ethanol.

(3) The thermodynamic optimization conditions obtained in this study are: the reaction temperature is 370-600 K, the reaction pressure is 3.0-9.0 MPa, H$_2$/HAC is 2.0-6.0, and the water content in raw material is minimized. Under the optimum conditions, the conversion effect of acetic acid and the selectivity of ethanol are all maintained at a better level.

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**Nomenclature**

$\text{RWGS}$ reverse water gas shift reaction

$F$ molar flow rate (mol/s)

$\text{MRS}$ multiple reaction system

$F_{(i)}$ molar flow rate of the ith carbonaceous component (mol/s)

$\text{SRS}$ simplified reaction system

$K_p$ equilibrium constant

$\text{CH}_3\text{COOH}$ HAC

$F_{(\text{out})}$ molar flow rate of the ith component in products (mol/s)

$\text{C}_2\text{H}_5\text{OH}$ EtOH

$S_{(i,c)}$ selectivity of the carbonaceous product

$\text{CH}_3\text{CHO}$ AH

$P$ pressure (MPa)

$\text{CH}_3\text{COOC}_2\text{H}_5$ EAC

$T$ temperature (K)

$\text{CH}_3\text{COCH}_3$ acetone

$X(\text{HAC})$ conversion rate of acetic acid

$\text{H}_2$/HAC the molar ratio of H$_2$/HAC

$\lambda$ the number of carbon atoms in the ith species in products

$\text{H}_2$/HAC the molar ratio of H$_2}$/HAC

$\Delta G_r$ Gibbs free energy change (kJ/mol)

$C_p$ specific heat at constant pressure (kJ/(mol $\cdot$ K))

$\Delta H_r$ reaction enthalpy change (kJ/mol)

$\gamma$ Stoichiometric number

$\Delta S_r$ reaction entropy change (kJ/mol)

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