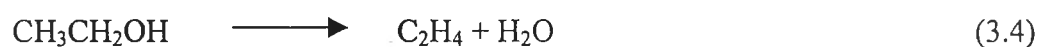
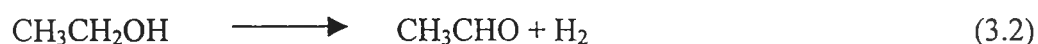
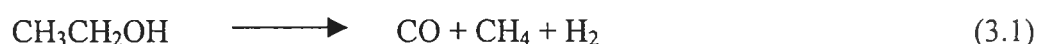


CHAPTER III

THEORY

Based on works reported on the literature, the overall ethanol decomposition reaction can be viewed as following reactions:



The reaction of ethanol decomposition occurred as a two-step process involving ethanol dehydrogenation (equation 3.2) followed by acetaldehyde decomposition (equation 3.3).

Ethanol decomposition is an acceptable reaction for fuel applications since it generates combustible gaseous products, see equation 3.1, which would assist the combustion process. Ethanol dehydration to form diethyl ether, equation 3.4, is also an acceptable side reaction while diethyl ether is a known fuel agent. Nevertheless, conditions that support ether formation may also support ethylene formation, equation 3.4. Ethylene in the product stream can cause rapid deactivation by coking of the catalyst, especially at low partial pressures of hydrogen. The focus of this section is to determine the feasibility of the ethanol decomposition reaction of fuel applications.

3.1 Thermodynamic calculation

The thermodynamic data can provide important information needed, i.e., the heat of reaction (ΔH_r^0) and the Gibbs free energy of equilibrium constant (K_p) from ΔG_r^0 . With the equilibrium constant known, the equilibrium product yield for a given set of reactions can be estimated.

Knowing the ΔG_r^0 values for all the potential surface reactions that may occur during the catalytic decomposition of ethanol over a temperature range of 100–1000°C allows us to determine the feasibility of a given reaction and to predict the expected equilibrium distribution of reactants and products. The thermodynamic feasibility of a reaction is defined by the criteria illustrated in Table 3.1.

Table 3.1: The criteria for thermodynamic feasibility

ΔG_r^0 (kcal.mol ⁻¹)	Feasibility
1. Very negative; < 10	Very high equilibrium conversion possible
2. Moderately negative; 0 to -10	Fairly high equilibrium conversion possible
3. Moderately positive; 0 to 10	Low equilibrium conversion depending upon process conditions
4. Very positive; > 10	Very low equilibrium conversion, generally not significant reactions

The ΔG_r^0 and ΔH_r^0 values for reactions (3.1), (3.4) and (3.5) are plotted versus temperature and the results are illustrated in Figures 3.1 and 3.2. The decomposition reaction, equation, (3.1) and one of the dehydration reactions, equation (3.4), are significantly endothermic while the dehydration reaction to form diethyl ether, equation (3.5), is exothermic.

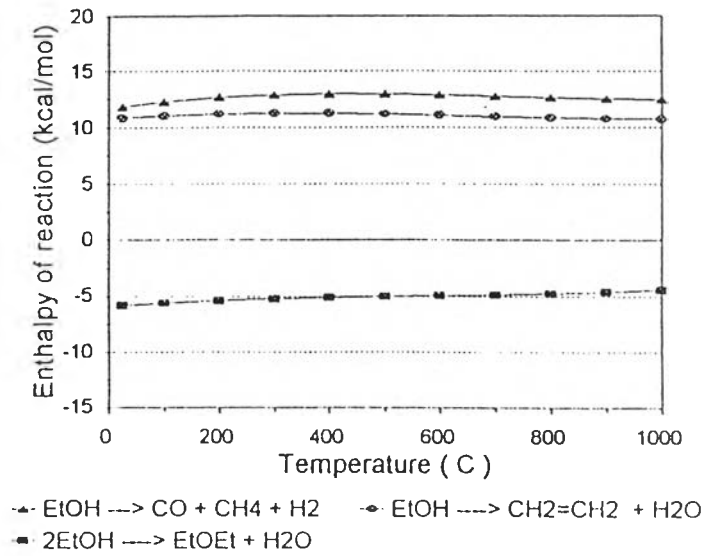


Figure 3.1 Enthalpy of reaction versus temperature for the ethanol decomposition and dehydration reactions.

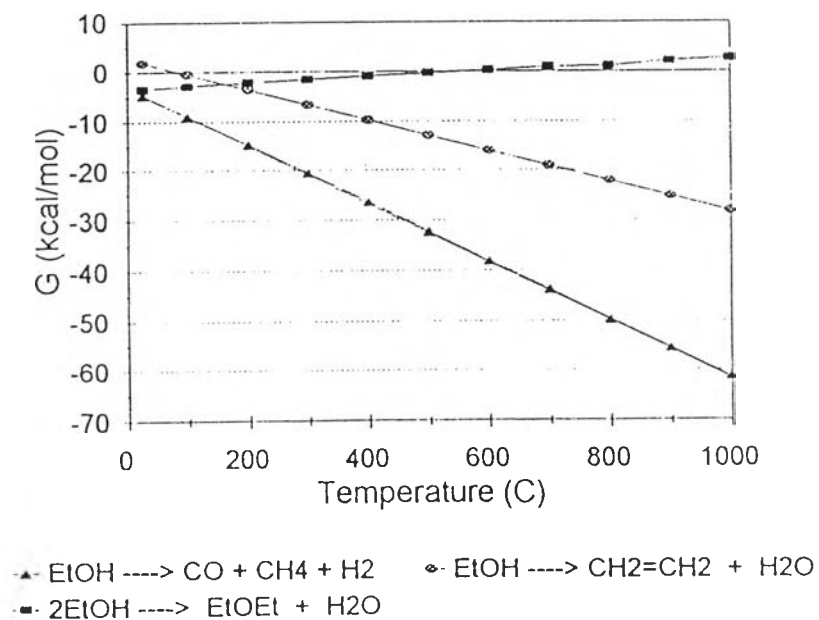


Figure 3.2 Gibbs free energy of reaction versus temperature for the ethanol decomposition and dehydration reactions.

The ΔG_r° values for the reactions (3.1), (3.4) and (3.5) are presented in Figure 3.2. All of the reactions are thermodynamically spontaneous between 100 and 500°C, which suggests the feasibility of good product yields. Ethylene formation becomes non-spontaneous below 100°C. Consequently, the temperatures that favor good equilibrium yields for the ethanol decomposition and diethyl ether formation reactions, and poor yields for the ethylene production, occur below 100°C. However, ethanol decomposition and diethyl ether production reactions would be kinetically limited at such low temperatures. Longsdon [20] reported that the rate of methanol decomposition is believed to be very low at temperatures below 200°C using metal supported catalysts. Ethanol decomposition is also expected to be kinetically limited in this temperature range.

Although the overall ethanol decomposition reaction is highly spontaneous, the reaction is thought to occur via a two-step process involving ethanol dehydrogenation, equation (3.2), and subsequent acetaldehyde decomposition, equation (3.3). If one of these steps is thermodynamically unfavorable, then the overall process may be limited by that reaction. The ΔG_r° and $\log K_{eq}$ values for these reactions were plotted versus temperature and the results are presented in Figure 3.3 and 3.4. Both reactions are spontaneous above 300°C; the equilibrium can be forced to the right if the subsequent decomposition reaction rapidly removes the acetaldehyde product from the first reaction nevertheless.

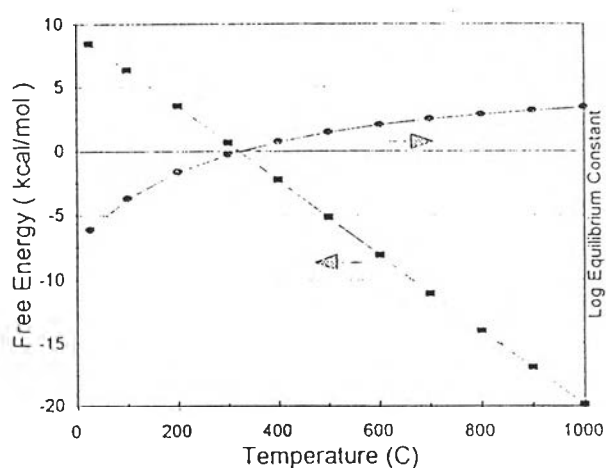


Figure 3.3 Gibbs free energy of reaction and log of the equilibrium constants for the ethanol dehydrogenation reaction.

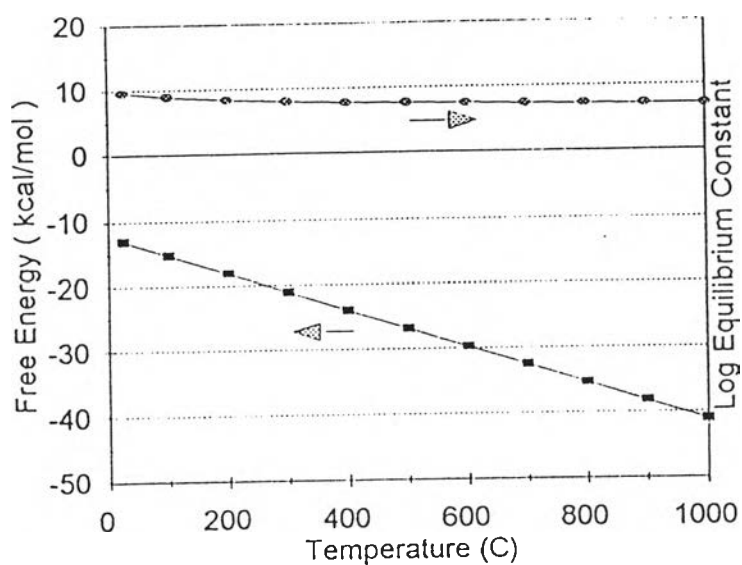


Figure 3.4 Gibbs free energy of reaction and log of the equilibrium constants for the acetaldehyde decomposition reaction.

In order to predict the equilibrium composition of the reactants and products, all possible side reactions must also be considered in addition to the obvious ones considered above. The additional side reactions considered are given in equation (3.6) through (3.8) below. Water may be introduced as an impurity in the ethanol feedstock or it may be generated in the catalyst bed via reactions (3.4) and (3.5). As shown in Figure 3.5, reaction (3.6) is thermodynamically favorable throughout the temperature range. Water may be reacting with CO, referred to as the water-gas shift reaction, equation (3.7), or it may react with methane via a steam reforming reaction, equation (3.8).



The ΔG_r° and $\log K_{eq}$ values for these side reactions involving water were plotted versus temperature and the results are presented in Figures 3.6 and 3.7. The water-gas shift reaction, equation (3.7), is thermodynamically favored at temperatures below 800°C, while the methane steam reforming reaction, equation (3.8), is favored at temperatures above 600°C to 800°C do both reactions appear to be spontaneous.

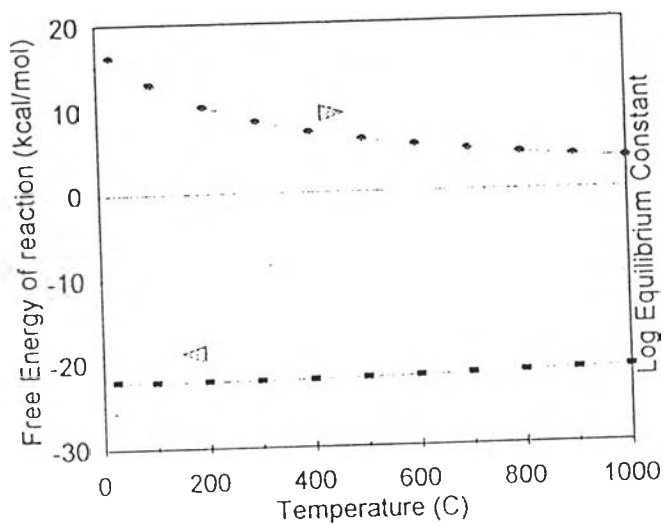


Figure 3.5 Gibbs free energy of reaction and log of the equilibrium constants for the reaction between ethanol and hydrogen.

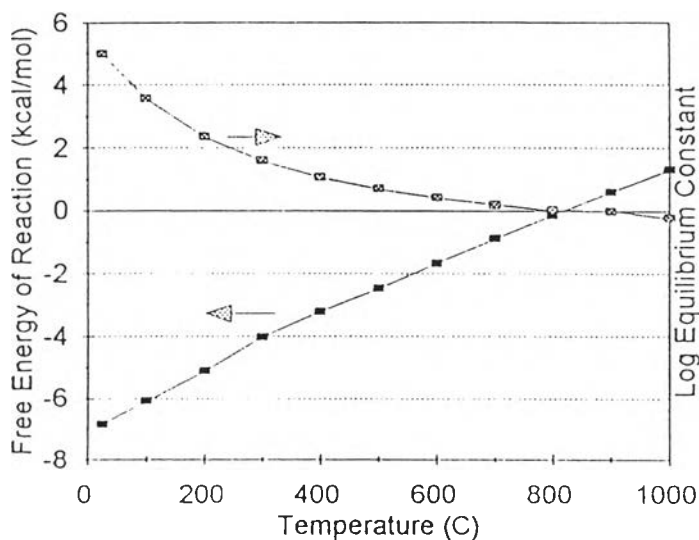


Figure 3.6 Gibbs free energy of reaction and log of the equilibrium constants for the water-gas shift reaction.

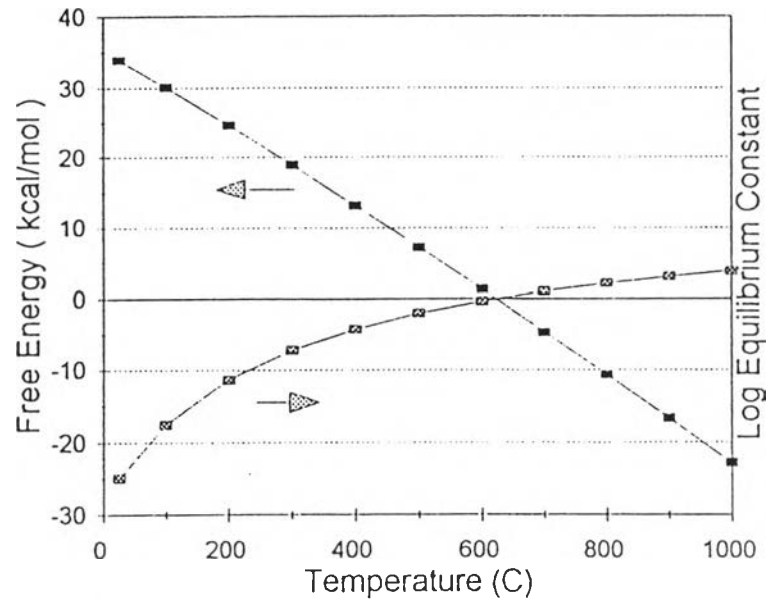


Figure 3.7 Gibbs free energy of reaction and log of the equilibrium constants for the methane stream reforming reaction.