

Research Article

Thermodynamic Equilibrium Analysis of Methanol Conversion to Hydrocarbons Using Cantera Methodology

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Reactions associated with removal of oxygen from oxygenates (deoxygenation) are an important aspect of hydrocarbon fuels production process from biorenewable substrates. Here we report the equilibrium composition of methanol-to-hydrocarbon system by minimizing the total Gibbs energy of the system using Cantera methodology. The system was treated as a mixture of 14 components which had CH_3OH , C_6H_6 , C_7H_8 , C_8H_{10} (ethyl benzene), C_8H_{10} (xylenes), C_2H_4 , C_2H_6 , C_3H_6 , CH_4 , H_2O , C , CO_2 , CO , H_2 . The carbon in the equilibrium mixture was used as a measure of coke formation which causes deactivation of catalysts that are used in aromatization reaction(s). Equilibrium compositions of each species were analyzed for temperatures ranging from 300 to 1380 K and pressure at 0–15 atm gauge. It was observed that when the temperature increases the mole fractions of benzene, toluene, ethylbenzene, and xylene pass through a maximum around 1020 K. At 300 K the most abundant species in the system were CH_4 , CO_2 , and H_2O with mole fractions 50%, 16.67%, and 33.33%, respectively. Similarly at high temperature (1380 K), the most abundant species in the system were H_2 and CO with mole fractions 64.5% and 32.6% respectively. The pressure in the system shows a significant impact on the composition of species.

1. Introduction

Methanol is the simplest alcohol which has a tremendous importance as an industrial feedstock [1, 2]. As a fuel, methanol does not have high enough specific heat value to compete with gasoline and therefore its not attractive as a substitute but as a motor fuel additive it is said to be improving the fuel quality. The prospect of methanol being used as raw material for fuel processing actually started with the accidental discovery by Chang and Silvestry in the early 70s [3]. With the use of newly discovered ZSM-5 it was found that methanol can be transformed to gasoline grade products. Methanol conversion process in the industry has branched into two paths, namely, methanol to olefins (MTO) and methanol to gasoline (MTG). Even though MTG got the global attention as an alternative route to produce fuel, it was unable to make the process economically viable [4, 5]. To make the process economical the process parameters has to be optimized. Catalyst upgrading to make deoxygenation reaction more selective toward gasoline

products such as benzene, toluene, ethylbenzene, and xylene (BTEX) is one such approach [6, 7]. Another approach is to alter the reaction conditions such as temperature, pressure, and residence time to augment the desired product spectrum [6, 8]. For this purpose, understanding the energetics of the MTG reaction pathway by thermodynamic analysis is also an important step.

The reaction pathway of MTG process is not yet completely resolved. However, from the available information in the literature, it is clear that it involves a series of reactions [9]. How the first C–C bond formation occurs is still under debate [10–12]. The widely accepted model so far is based on the hydrocarbon pool method where it is described as a catalytic scaffold with organic molecules adsorbed on to the zeolite structure [13, 14].

As given in Figure 1, MTG process takes place in a series of steps where formation of dimethyl ether is said to be the first step. Olefinic products produced at the secondary stage is significant for the MTO process while at tertiary stage is gasoline grade products are obtained. The products of MTG

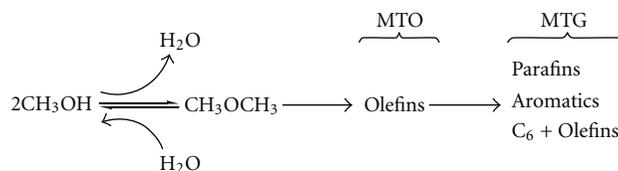


FIGURE 1: Reaction pathway of MTO and MTG processes as proposed in the literature [15].

process consists of a mixture of paraffins, aromatics, and olefins, and for the thermodynamic system, are treated as equilibrium products in this analysis.

2. Thermodynamic Equilibrium Analysis

If the stoichiometric equation of methanol conversion to aromatic hydrocarbons is known, the thermodynamic equilibrium analysis can easily be performed using the equilibrium constant. However, when the reaction stoichiometry is not known, the nonstoichiometric method should be used. Equilibrium composition for nonstoichiometric systems can be determined by different methods such as energy minimization technique, kinetic/dynamic model, or by neural network technique. Since our system involves temperature and pressure as variables, it is much convenient to select Gibbs free energy minimization technique. In this study, a code written in Python (an open source programming language) to run the Cantera software library was used to analyze the equilibrium composition of the model mixture. Cantera is an object oriented software tool developed by a team from California Institute of Technology for solving chemical kinetics, thermodynamics, and transport processes [16]. Equilibrium composition was determined by Gibbs energy minimization by the Villars-Cruise-Smith algorithm [17]. Thermodynamic data for the species were calculated using the nine-coefficient NASA polynomial [18]. All the coefficients for the polynomial were obtained from Burcats online database [19].

3. Results and Discussion

The outcome of the optimization routine is the mole fraction of each of the fourteen compounds in the mixture at each pressure and temperature. Since it is a gas phase system, the partial pressure of each component is proportional to mole fraction and results are analyzed in those terms. As expected, the system with the fourteen components reaches equilibrium at different temperatures and pressures.

The key input to the model was the standard formation enthalpies of different species considered. Table 1 gives the formation enthalpies as obtained from [20].

3.1. Methanol Conversion to Aromatics. According to the thermodynamic analysis, equilibrium aromatics yield at different temperatures is extremely low. Figure 2(a) depicts that the BTEX mole fraction trend in the equilibrium mixture passes through a maximum around 1100 K. The mole fraction of BTEX clearly increases as pressure increases.

TABLE 1: Standard formation enthalpies of the species considered in the system.

Compound name	ΔH_f° (kJ/kmol)
CH ₃ OH	-205
C ₆ H ₆	82.8
C ₇ H ₈	50.1
C ₈ H ₁₀ (ethyl benzene)	49.0
C ₈ H ₁₀ (xylenes)	17.9
C ₂ H ₄	52.47
C ₂ H ₆	-83.8
C ₃ H ₆	20.41
CH ₄	-74.87
H ₂ O	-241.83
C	0.0
CO ₂	-393.52
CO	-110.53
H ₂	0.0

The reaction model considered in this study resembles a thermochemical conversion of methanol at different pressures. It is interesting to note that all the aromatics considered in the model initiated formation around 850 K and peaked approximately around 1110 K. The formation started to disappear beyond 1300 K.

This analysis suggests that to maximize gasoline fraction aromatic products formation, the reactions should be carried out at a narrow temperature regime. This temperature window broadens as pressure increases but is quite narrow at lower pressures. It appears that the best reaction temperature for gasoline range aromatics formation is around 800–850 °C.

In order to better approximate experimental BTX yields the model was forced to reach equilibrium with eleven hydrocarbon products such as CH₃OH, C₆H₆, C₇H₈, C₈H₁₀ (ethyl benzene), C₈H₁₀ (xylenes), C₂H₄, C₂H₆, C₃H₆, CH₄, H₂O, H₂ neglecting thermodynamically more stable species such as CO₂, CO, and C. This forced equilibrium conditions resulted in changing the aromatic mole fraction in the system significantly as shown in Figure 2(b). According to this analysis, the highest total aromatic mole percentage of 9.41% was observed at 0 psi and 1380 K. Thermodynamics favor benzene formation in both methods in the aromatic fraction and the highest yield is reported at 0 psi and 1380 K.

3.2. Methanol Conversion to Paraffins. Methane, ethane, and propane are the alkanes considered in this model. It is quite

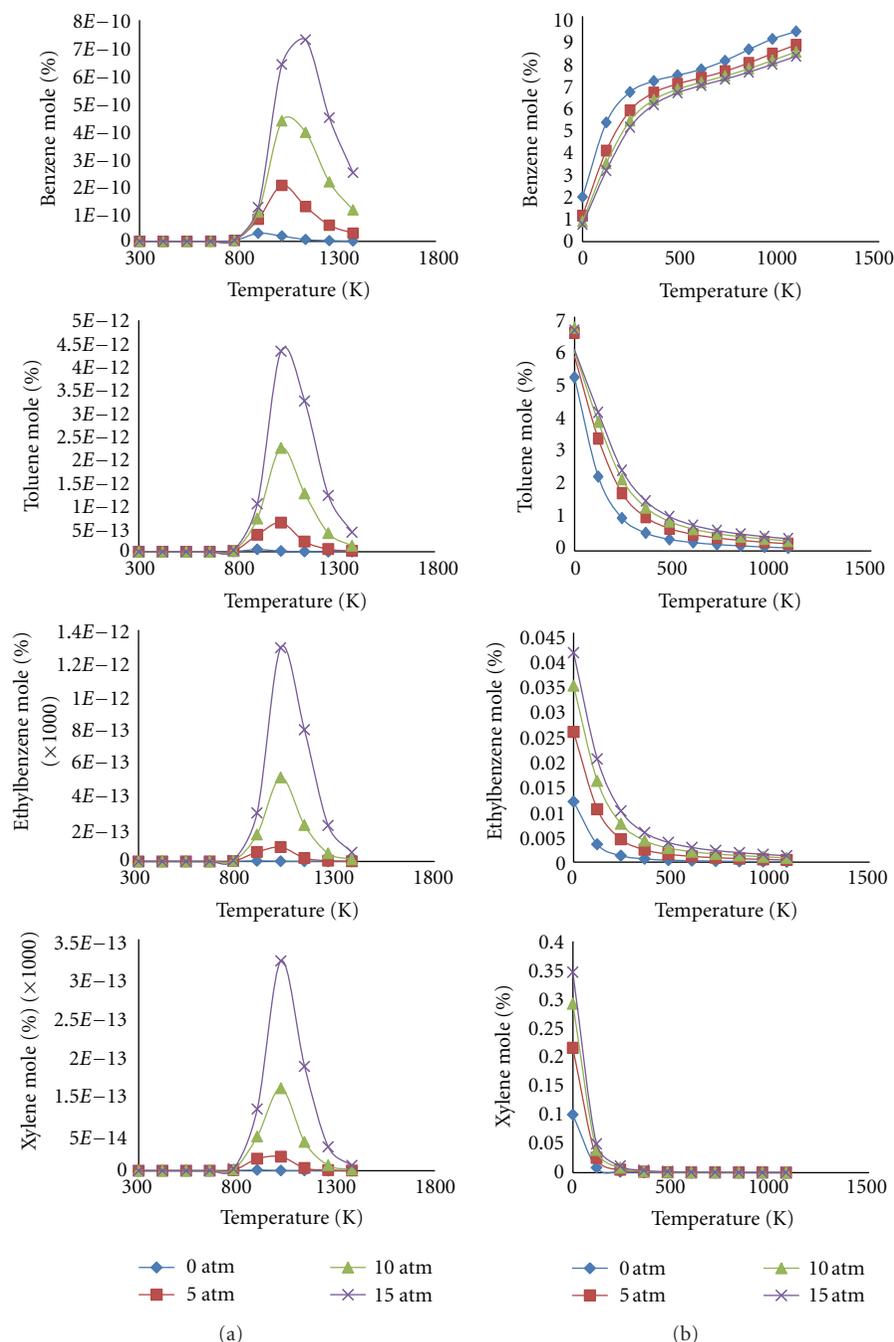


FIGURE 2: (a) Equilibrium composition of gasoline-range aromatic hydrocarbons in the fourteen-component model. (b) The equilibrium composition of aromatics after the system was forced to equilibrate with eleven species removing CO₂, CO, and C.

interesting that methane is the most abundant alkane in the equilibrium mixture at 300 K under both models that were tested.

Molar fraction of ethane is relatively low, but, shows an interesting behavior with respect to temperature and pressure (Figure 3). Increasing pressure increases the mole fraction of ethane and with increasing temperature, the trends is to pass through a maximum around 900 K–1120 K. According to the unrestricted model, propane mole

percentage in the equilibrium mixture is very low—including the forced equilibrium model. The analysis indicates that methane is the only alkane, that is, thermodynamically favorable.

3.3. Methanol Conversion to Olefins. In this thermodynamic model, we have considered ethylene which has been reported to be present when methanol is catalytically processed [6]. It is widely believed that ethylene is one of the preliminary

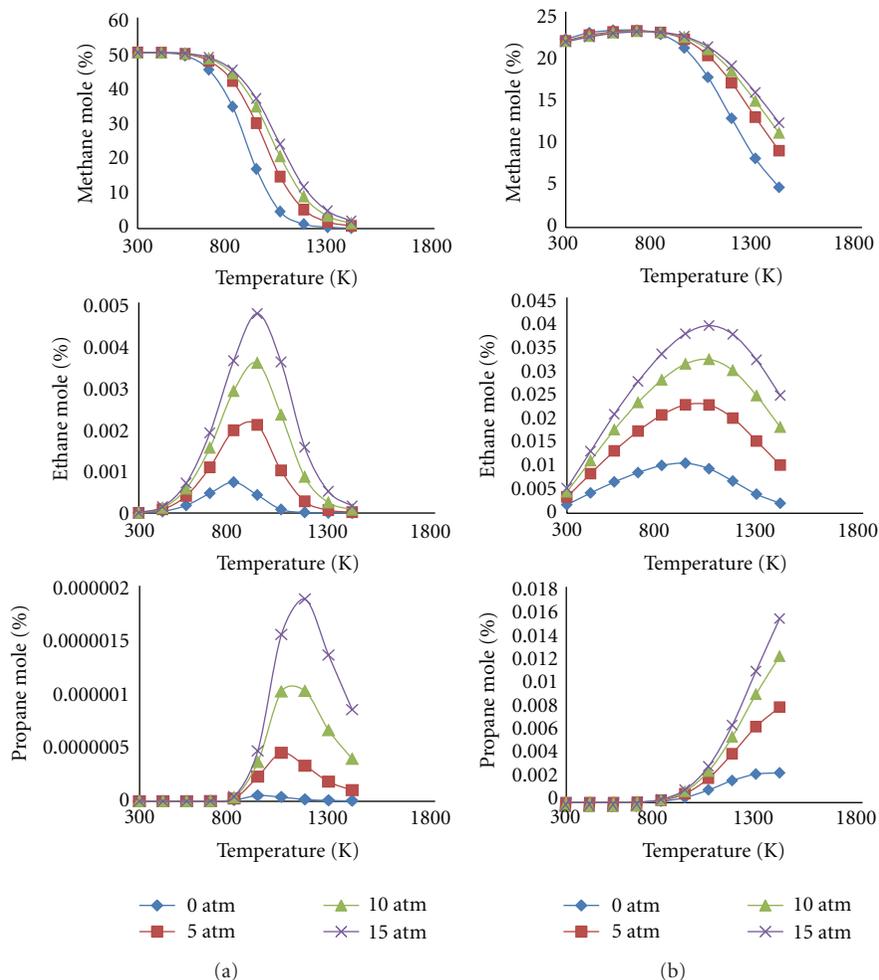


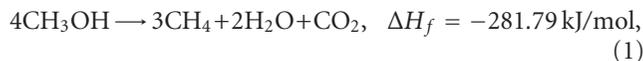
FIGURE 3: Equilibrium mole fractions of paraffins (a) with thermodynamically stable species considered in the model, (b) when CO_2 , CO , and C dropped from the model.

products when methanol is converted in the presence of catalyst such as ZSM-5. However, according to Figure 4(a), it is clear that in the equilibrium mixture, the mole percentage of ethylene is quite low but under the forced equilibrium ethylene shows a significant presence than ethane and propane. It is clear that under both models, the increase of temperature clearly favored formation of ethylene.

3.4. Formation of Solid Carbon and Syngas. Carbon that is produced in the reaction is commonly attributed as a cause for catalyst deactivation. It can be seen from Figure 5(a) that carbon formation varies significantly as the temperature increases but the equilibrium mole percents are extremely low. Accordingly, the effect of pressure on carbon formation is not significant. It should be noted that in practice, the coke formation can happen not only as a result of direct carbon deposition but also by deposition of larger molecular weight carbonaceous compounds on active sites of the catalyst.

Under unrestricted equilibrium conditions, two reaction schemes can be proposed for the system. At low temperatures (300–500 K) the most abundant species in the system are

methane, water, and carbon dioxide. All the other species in the model can be neglected since these are present in extremely low concentrations at these temperatures. This reaction is depicted in stoichiometric form in (1). The heat of reaction which amounts to -281.79 kJ/mol indicates that it is highly exothermic and the products methane, water, and carbon dioxide are the most stable at low temperatures. Similarly, at higher temperatures the most abundant and the most stable species are carbon monoxide and hydrogen. Hydrogen is present in the highest concentrations at temperatures $> 1000 \text{ K}$ in the mixture which amounts to 66.1% in the unrestricted equilibrium model. The products (formed at high temperature environment) can be represented in a stoichiometric form as shown in (2):



The system with fourteen species attains thermodynamic equilibrium at different temperatures and pressures. At

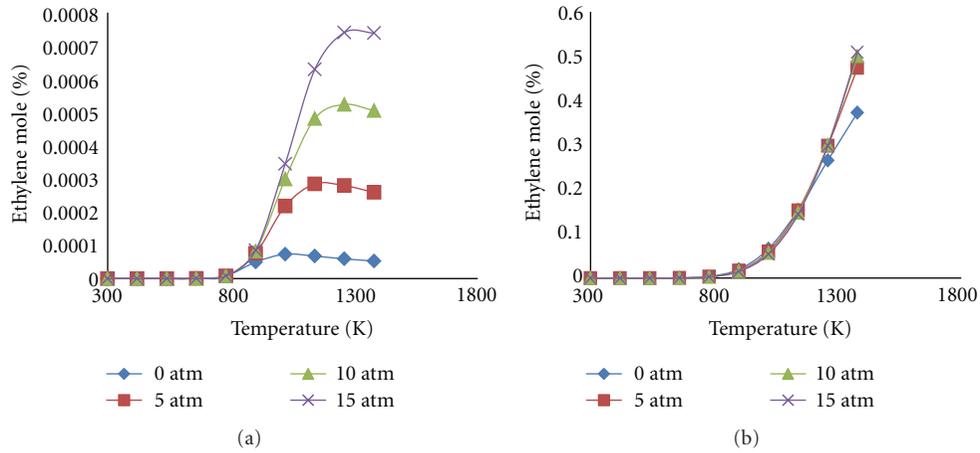


FIGURE 4: Variation of carbon mole fraction with respect to temperature at different pressures.

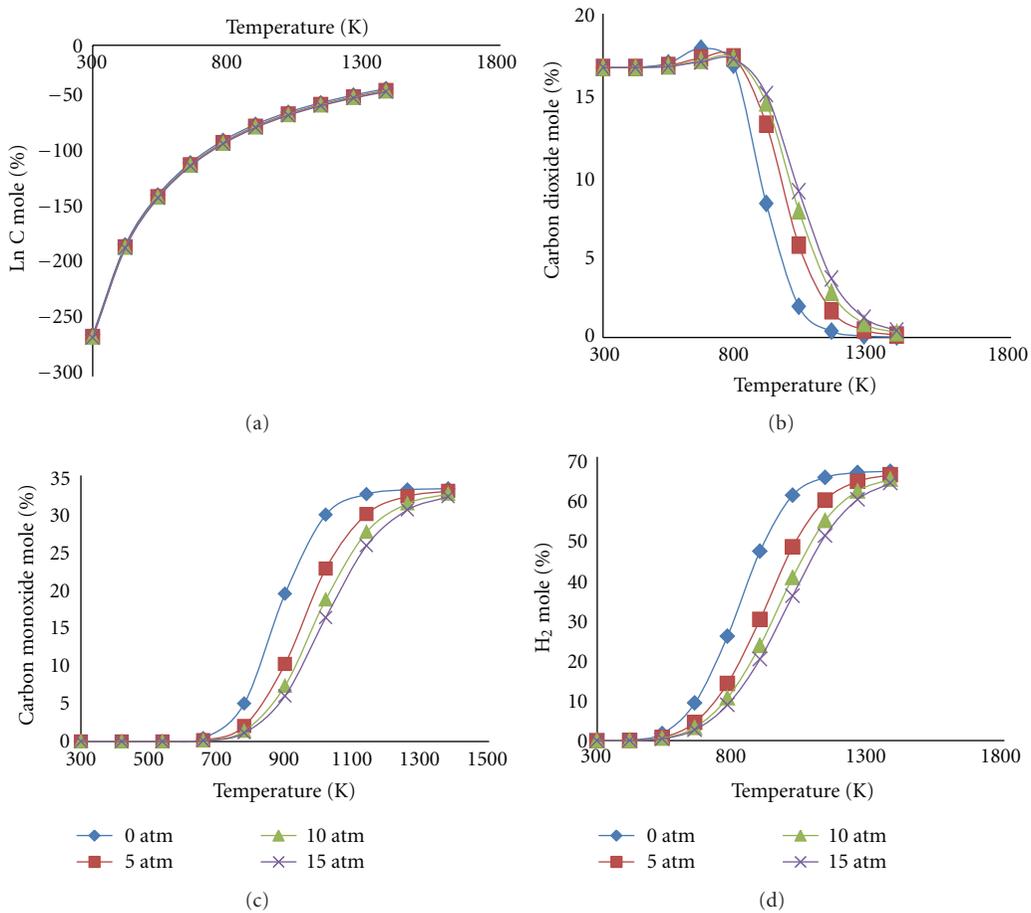


FIGURE 5: Variation of (a) carbon, (b) carbon dioxide, (c) carbon monoxide, (d) hydrogen, mole fraction with respect to temperature at different pressures.

equilibrium, the overall ΔG of the mixture is a measure of how stable the reaction is at respective reaction conditions. According to Figure 6, the Gibbs free energy of the system stays in negative region implying that the reaction is spontaneous. As the temperature increases the negative

value of ΔG increases and reaches a minimum around 780 K.

For this system under equilibrium, an equilibrium constant can be calculated using (3). According to Figure 7, the system has a large equilibrium constant. A reaction with

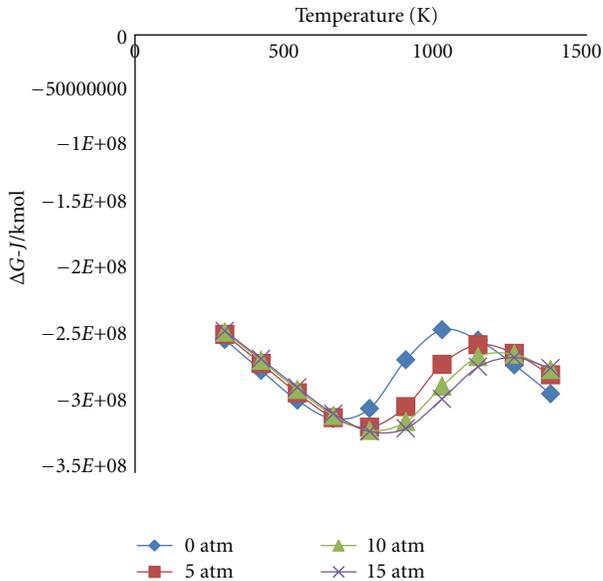


FIGURE 6: Variation of the total Gibbs free energy of the reaction (ΔG_{rx}°) with respect to temperature at different pressures.

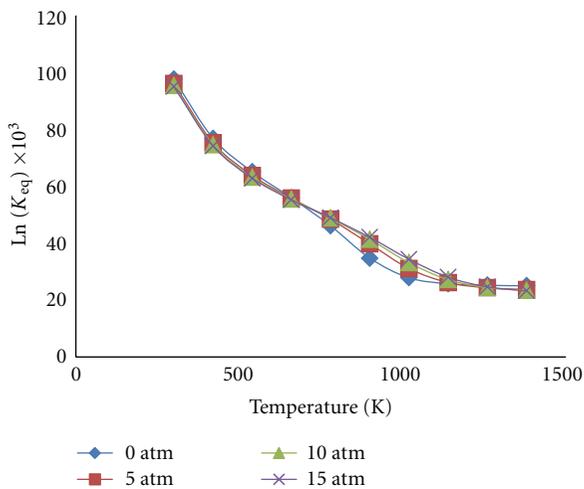


FIGURE 7: Variation of the equilibrium constant of the system with respect to temperature at different pressures.

a large equilibrium constant can take a long time to reach the equilibrium depending on the kinetics of the reaction. As the temperature increases the equilibrium constant reduces exponentially:

$$K_a = \exp\left(\frac{-\Delta G}{RT}\right). \quad (3)$$

The overall analysis suggests that when this mixture is left to equilibrate at the temperature and pressure conditions specified, the tendency of the system is to favor formation of low molecular weight compounds (such as CH_3 , CO , CO_2 , H_2 , and H_2O). Although in a liquid fuel production point of view, we anticipate obtaining high yields of hydrocarbons,

this analysis suggests that the equilibrium mole percent of BTEX can reach up to 9.41%. This observation could be reinforced by the fact that ΔH_f for BTEX are all positive, the system tends to favor formation of more stable compounds with more negative ΔH_f values [21]. Accordingly, it is clear that at higher temperatures, in the absence of a catalyst, the tendency of methanol is to produce a Syngas containing primarily CO and H_2 . However, literature suggests that the dynamics of the reaction changes in the presence of a catalyst such as ZSM-5. It has been shown that in the presence of a catalyst under analogous conditions, significant amounts of BTEX (with ethylene and xylenes having the highest selectivities) are produced [6]. The inference of this analysis is that, in the presence of a catalyst, simultaneous formation of all considered molecules does not occur from methanol; rather, independent reactions that comprise of only a few selected intermediate products may occur. However, with sufficient time, these energetically favorable intermediates will break down to more stable low molecular weight compounds.

4. Conclusions

Two models were tested to understand the behavior of aromatics, alkanes, and alkenes production when methanol is thermochemically deoxygenated. Under the forced equilibrium conditions it shows that the aromatic mole percentage is 9.41%. At low temperature the most abundant stable species were methane, carbon dioxide, and water, while hydrogen and carbon monoxide were the most dominant stable species at higher temperatures. Methane was the most abundant species at low temperature with a mole fraction of 50%. At high temperature the most abundant species was hydrogen with mole fraction 66.1%. The system under equilibrium produces negligible amounts of elemental carbon. The negative values of the free energy (ΔG) of the system indicate that the reaction is spontaneous for the entire range of temperatures pressures that were analyzed. Further, the analysis indicates that increasing temperature would increase the negative value of free energy making the system stable. The overall equilibrium constant of the system drops exponentially with increasing temperature.

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