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Thermodynamic analysis of glycerol conversion to synthesis gas

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Introduction

Glycerol is a very useful raw material. Its unique structure, properties, bioavailability and renewability bring out a lot of possibilities for the conversion [1]. Nowadays the significant quantities of glycerol are produced during the transestrification of vegetable oils into biodiesel. Glycerol is the main side-product of mentioned reaction. It is equivalent to approximately10 wt. % of the total produced biodiesel [2,3].
Numerous pathways of glycerol conversion into valuable compounds including surfactants, acrolein, glycerol carbonates, fuel additives etc. were explored [4]. A very interesting solution for glycerol utilization is its conversion either to synthesis gas or hydrogen. Both mentioned have many application in the chemical synthesis, for example: methanol - the fundamental component in the vegetable oils transestrification. In addition, the synthesis gas can be also used in Fischer-Tropsch reactions [5].
Some thermodynamic investigations concerning this problem have been carried out. They are very important because of furnishing some information about conditions of synthesis gas production with fixed composition. The analyses run in this manner are good introduction to the next experiments.

Experimental

In this study, thermodynamic analysis of glycerol conversion to synthesis gas has been considered. The calculation were done for three different models of glycerol conversion. The literature data have been shown that the main reagents in the process of glycerol conversion with/without carbon dioxide are: glycerol, carbon monoxide, hydrogen, carbon dioxide, water and methane. Considering these reagents, the number of linear independent reactions was calculated. The method of atomic coefficients was used. It follows from the calculations that to describe process of glycerol conversion, it is necessary to take into consideration three linear independent reactions (when here are six components. In table 1 selected stoichiometric models are presented.

Table 1: The selected stoichiometric models.

1st model	2nd model	3rd model
$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2$	$C_3H_8O_3 + CO_2 = 4CO + 3H_2 + H_2O$	$C_3H_8O_3 = 3CO + 4H_2$
$CO_2 + H_2 = CO + H_2O$	$CO_2 + H_2 = CO + H_2O$	$CO + 3H_2 = CH_4 + H_2O$
$CO_2 + 4H_2 = CH_4 + 2H_2O$	$CO + 3H_2 = CH_4 + H_2O$	$CO + H_2O = CO_2 + H_2$

In the first model glycerol was converted with steam (steam reforming), in the second with carbon dioxide (dry reforming), while in the last one without any co-substrates. The calculation were carried out in the 600-1000 K temperature and 1-30 atm ranges. The effect of mol composition of feed mixture was analyzed as well.
All of calculations were made in Mathcad 14.0, while the thermodynamic values were taken from database of Chemcad 2.60I.

Results and Discussion

The number of publications concerning thermodynamic analysis of glycerol conversion to synthesis gas is rather limited. Wang and co-researchers [6] have concentrated their attention to equilibrium composition for assumed model of glycerol conversion with CO_2. The minimalization method of Gibbs free energy has been used in their calculations. In solving this problem the following reactions have been chosen:

$C_3H_8O_3 = 4H_2 + 3CO$ (1)
$CO + 3H_2 = CH_4 + H_2O$ (2)
$CO_2 + 4H_2 = CH_4 + 2H_2O$ (3)
$CO_2 + CH_4 = 2H_2 + 2CO$ (4)
$CO + H_2O = H_2 + CO_2$ (5)
$C + H_2O = H_2 + CO$ (6)
$CH_4 = 2H_2 + C$ (7)
$2CO = CO_2 + C$ (8)
$C + 2H_2O = 2H_2 + CO_2$ (9)

In the first reaction, the high value of equilibrium constant entails necessity of introducing an assumption of total glycerol conversion. The analysis was made for the temperature range 600-1000 K for 1 atm and 3 atm. The amount of synthesis gas increases with the temperature rise and molar ratio of $CO_2/C_3H_8O_3$. On the other hand, the researchers [7] have been made some calculations for the glycerol conversion with steam. The equilibrium composition was also determined by stoichiometric method. This work presents the influence of variable parameters like pressure, temperature and the initial molar ratio of $H_2O/C_3H_8O_3$ on equilibrium composition of products. The simplified model used in the calculations is presented below:

$C_3H_8O_3 = 4H_2 + 3CO$ (1)
$CO + H_2O = H_2 + CO_2$ (5)
$CO + 3H_2 = CH_4 + H_2O$ (2)

The following working hypothesis was adopted: the value of conversion degree of glycerol averages 1. The temperature of the process ranged from 600 to 1200 K. Additionally, the pressures were also varied (1 atm, 3 atm, 6 atm and 9 atm). It follows from the experiments that high temperature and high value of molar ratio - $H_2O/C_3H_8O_3$ – favor hydrogen formation. The significant content of steam in the feed limits methane production.
In our work, thanks to thermodynamic calculations of glycerol conversion in presence/absence of CO_2 or with steam, it is possible to obtain some useful information. In the all cases of glycerol conversion to synthesis gas, the most beneficial conditions of conducting process are high temperature (> 800 K) and low pressures owing to the biggest part of hydrogen and carbon monoxide in the equilibrium mixture.
The mixture, rich in hydrogen can be obtained in the process of glycerol conversion with steam (1^{st} model). In the range of temperature 600-1000 K (at P = 1 atm), the molar ratio of CO/H_2 undertakes values from 0,01 to 0,29. Conversion of glycerol with carbon dioxide (2^{nd} model) gives gaseous product abundant with carbon monoxide. The equilibrium molar ratio of CO/H_2 depends on temperature and over 800 K – also on pressure. The value of CO/H_2 increases from 0,50 to 1,76 while the temperature rises from 600 to 1000 K. When the process is carried out without carbon dioxide or steam (3^{rd} model), high methane concentration is observed in the equilibrium mixture. Our calculation are in good agreement with the literature data.

Conclusions

It was found that the contribution of synthesis gas in the equilibrium mixture increases with the increase temperature. Moreover, the calculations indicate that conversion of glycerol should be carried out under low pressure and at above 800 K temperature. Moreover, in the steam reforming of glycerol synthesis gas rich with hydrogen is produced, while in the dry reforming the carbon monoxide predominates in the equilibrium mixture.

References

[1]. Ch.-H. (Clayton) Zhou, J. N. Beltramini, Y.-X. Fan and G. Q. (Max) Lu, *Chem. Soc. Rev.*,37 (2007) 527-549.
[2]. F. Frusteri, F. Arena, G. Bonura, C. Canilla, L. Spadaro, O. Di Blasi, *Appl. Catal. A*, 367 (2009) 77-83.
[3]. J.A. Melero, G. Vincente, G. Morales, M. Paniagua, J.M. Moreno, R. Roldan, A. Ezquerro and C. Perez, *Appl. Catal. A*, 346 (2008) 44-51.
[4]. J. Barrault, F. Jerome, *Eur. J. Lipid Sci. Technol*., 110 (2008) 825-830.
[5]. A.Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem*.,10 (2007) 13-20.
[6]. X. Wang, M. Li, M. Wang, H. Wang, Sh. Li, Sh. Wang, X. Ma, *Fuel* 88 (2009) 2148–2153.
[7]. M. L. Dieuzeide, N. Amadeo, *Chem. Eng. Technol.*,33 (2010) 89–96.