# Renewable hydrogen production methods based on biomass processing

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# Thesis objectives

- Thermodynamic study of hydrogen production via bioethanol catalytic steam reforming
- Kinetic modeling of bioethanol catalytic steam reforming
- Analysis of different types of concepts of 100MW thermal power production from bioethanol
- Thermodynamic analysis of hydrogen production via bioglycerol catalytic steam reforming
- Kinetic modeling of bioglycerol catalytic steam reforming
- Analysis of different types of concepts of 100MW thermal power production from bioglycerol
- Dynamic simulation of hydrogen production from bioglycerol steam reforming in continuous tubular reactor

# Achived results

# Thermodynamic study of hydrogen production via bioethanol catalytic steam reforming

- Thermodynamic analysis is important before implementing a new process flow, because must know the most important parameters that influence the new process.

- In the calculation of the gaseous mixture composition at equilibrium a mathematical model developed in CHEMCAD process simulator was used.

# The most important reaction for bioethanol steam reforming

1. $CH_3CH_2OH + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2$
2. $CH_3CH_2OH + H_2O \rightarrow 4\ H_2 + 2\ CO$
3. $CO + H_2O \rightarrow CO_2 + H_2$
4. $CH_3CH_2OH \rightarrow H_2 + CO + CH_4$
5. $CO + 3\ H_2 \rightarrow CH_4 + H_2O$
6. $CH_3CHO + 3\ H_2O \rightarrow 5\ H_2 + 2\ CO_2$
7. $CH_3COCH_3 + 3\ H_2O \rightarrow 3\ CO + 6\ H_2$
8. $CH_3COOH + 2\ H_2O \rightarrow 2\ CO_2 + 4\ H_2$
9. $CH_3CH_2OH \rightarrow H_2 + CH_3CHO$
10. $CH_3CH_2OH \rightarrow C_2H_4 + H_2O$
11. $CH_3CHO \rightarrow CH_4 + CO$
12. $C_2H_4 \rightarrow 2\ C + 2H_2$
13. $2\ CO \rightarrow CO_2 + C$

Zsolt Tasnadi-Asztalos, Ana-Maria Cormos, Árpád Imre-Lucaci, and Clin C. Cormos, **Thermodynamic Evaluation of Hydrogen Production via Bioethanol Steam Reforming,** AIP Conference Proceedings **1565**, 175 (2013)

# Results of thermodynamic study via bioethanol steam reforming

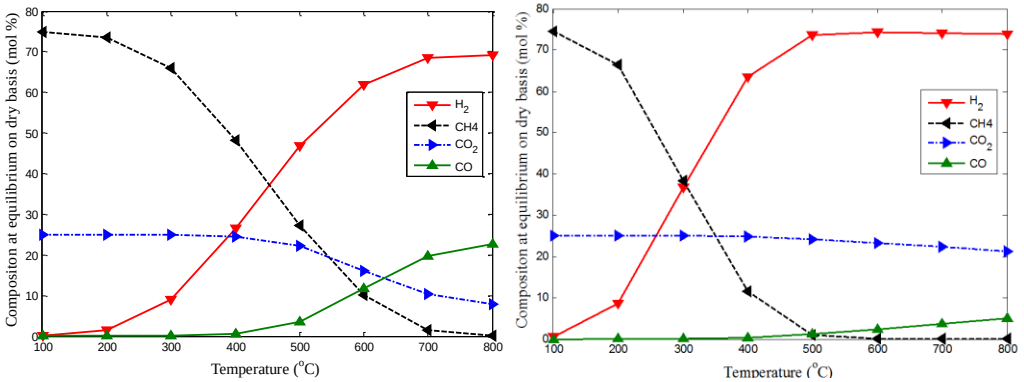
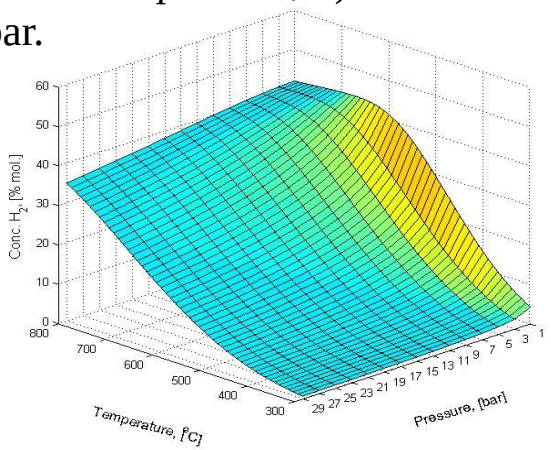
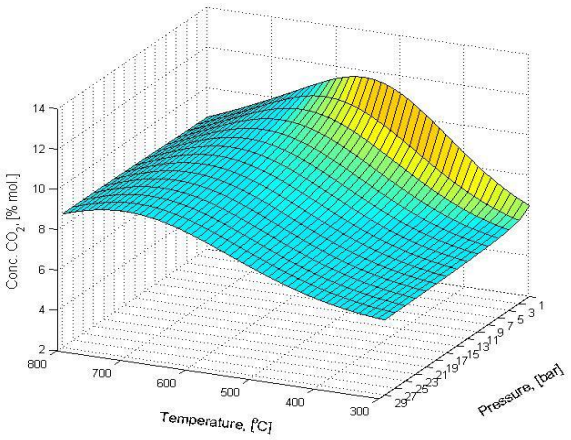



**FIGURE 1.** Composition at equilibrium reported to dry gas function of temperature at: a) *r*=3 and *p*=1 bar; b) *r*=25 and *p*=1 bar.




2.a) 2.b)

Concentration profiles at equilibrium for the major products of the bioethanol stream reforming process at *r*=25.

Zsolt Tasnadi-Asztalos, Ana-Maria Cormos, Árpád Imre-Lucaci, and Clin C. Cormos, **Thermodynamic Evaluation of Hydrogen Production via Bioethanol Steam Reforming,** AIP Conference Proceedings **1565**, 175 (2013)

# Kinetic study of bioethanol catalytic steam reforming

There are few papers in the literature on kinetic studies of ethanol steam reforming, because the system is complex. Some kinetic studies have been published in which power law, Eley Rideal (ER), Langmuir Hinshelwood (LH) and Langmuir-Hilnshinwood-Hougen-Watson-(LHHW) model kinetic expressions are reported.

# Kinetic model parameters

Table1.Kinetic parameters with we started the optimization

| $k_{i(T)} = k_{i(898.15K)}\, e^{-(Ea,i/R)\,((1/T)-(1/898.15\ K))}$ [mol/min mg]<br>$K_{i(T)} = K_{i(898.15K)}\, e^{-(\Delta Hi/R)\,((1/T)-(1/898.15\ K))}$ [dimensionless] | | $Ea_i$, $\Delta H_i$ [kJ/mol] | |
|---|---|---|---|
| $k_{E1,(898.15K)}$ | $1.13 \cdot 10^{-7}$ | $Ea_{E1}$ | 122.9 |
| $k_{E2,(898.15K)}$ | $3.06 \cdot 10^{-7}$ | $Ea_{E2}$ | 195.5 |
| $k_{R1,(898.15K)}$ | $2.48 \cdot 10^{-3}$ | $Ea_{R1}$ | 174.0 |
| $k_{R2,(898.15K)}$ | $9.12 \cdot 10^{-4}$ | $Ea_{R2}$ | 166.3 |
| $K_{Et(898.15K)}$ | $8.76 \cdot 10^{-27}$ | $\Delta H_{Et}$ | –601.4 |
| $K_{CHO(898.15K)}$ | $2.10 \cdot 10^{-1}$ | $\Delta H_{CHO}$ | –410.4 |
| $K_{CH2(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{CH2}$ | –118.4 |
| $K_{CH(898.15K)}$ | $3.05 \cdot 10^{-1}$ | $\Delta H_{CH}$ | –360.7 |
| $K_{CH3(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{CH3}$ | –126.8 |
| $K_{H2(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{H2O}$ | –83.1 |
| $K_{OH(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{OH}$ | –145.5 |
| $K_{CH4(898.15K)}$ | $6.34 \cdot 10^{-18}$ | $\Delta H_{CH4}$ | –86.1 |
| $K_{CO(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{CO}$ | –83.1 |
| $K_{H(898.15K)}$ | $8.76 \cdot 10^{-27}$ | $\Delta H_{H}$ | –247.4 |
| $K_{CO2(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{CO2}$ | –83.4 |
| $K_{H2(898.15K)}$ | $1.93 \cdot 10^{-22}$ | $\Delta H_{H2}$ | –931.2 |

Table2.Global kinetic coefficient after optimization

| Parameters | Calculated parameters |
|---|---|
| | Exp 1-5 |
| $k_{E1sim}$ | $3.64*10^{-5}$ |
| $k_{E2sim}$ | $1.44*10^{-5}$ |
| $k_{R1sim}$ | $0.55*10^{-3}$ |
| $k_{R2sim}$ | $4.33*10^{-2}$ |

**Zsolt Tasnádi-Asztalos[a], Árpád Imre-Lucaci[a], Ana-Maria Cormoş[a], Mihaela Diana Lazăr[b], Paul-Şerban Agachi[a], Thermodynamic Study and Kinetic Modeling of Bioethanol Steam Reforming,** Studia UBB Chemia, LVIII, 4, 2013

# The results of kinetic model of bioethanol catalytic steam reforming

Table3. Experimental and calculated values of components concentration

| Comp. | Θ | | | | | | | | | | $\bar{\varepsilon}_2$ % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\theta_1$ | | $\theta_2$ | | $\theta_3$ | | $\theta_4$ | | $\theta_5$ | | |
| | Exp | Calc | Exp | Calc | Exp | Calc | Exp | Calc | Exp | Calc | |
| $H_2$ | 0.02 | 0.07 | 0.03 | 0.07 | 0.10 | 0.08 | 0.26 | 0.26 | 0.44 | 0.36 | 35.2 |
| $H_2O$ | 0.94 | 0.88 | 0.89 | 0.88 | 0.83 | 0.86 | 0.61 | 0.48 | 0.24 | 0.27 | 9.9 |
| $CO_2$ | 0.01 | 0.03 | 0.01 | 0.03 | 0.04 | 0.04 | 0.08 | 0.13 | 0.16 | 0.18 | 36.6 |
| $CH_4$ | $1 \cdot 10^{-3}$ | 0.01 | $2 \cdot 10^{-3}$ | 0.01 | 0.04 | 0.02 | 0.04 | 0.13 | 0.12 | 0.18 | 74.5 |
| $\bar{\varepsilon}_1$ % | 58.7 | | 51.2 | | 32.1 | | 33.7 | | 19.4 | | |

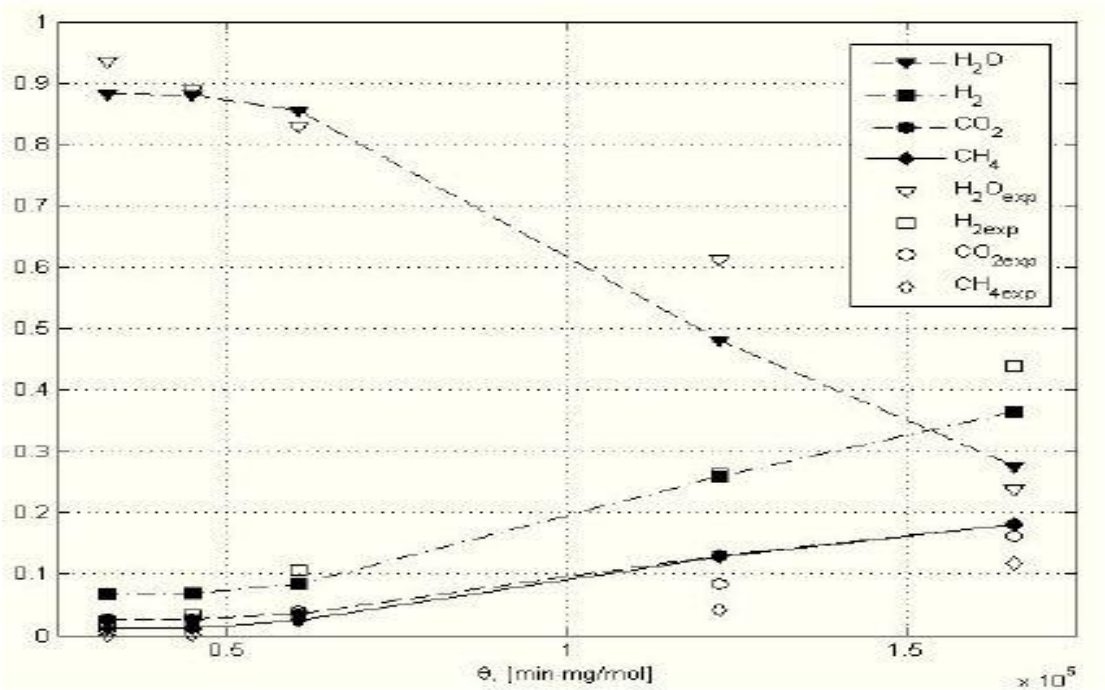



Figure3. Measured and simulation data of steam reforming of bioethanol (with symbols are shown the experimental data and with lines and symbols the simulation results)

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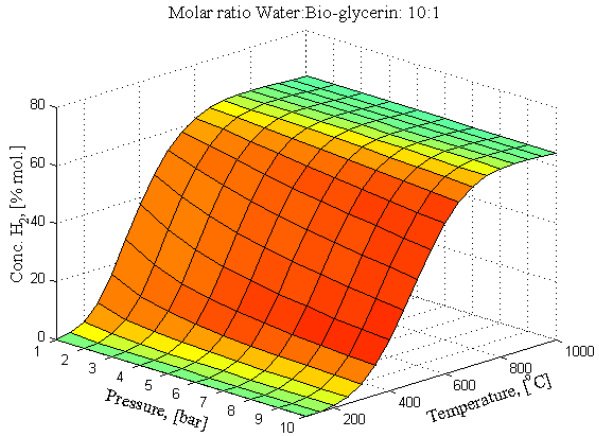
# Thermodynamic study of hydrogen production via bioglycerol catalytic steam reforming

The main reaction of bioglycerol catalytic steam reforming:

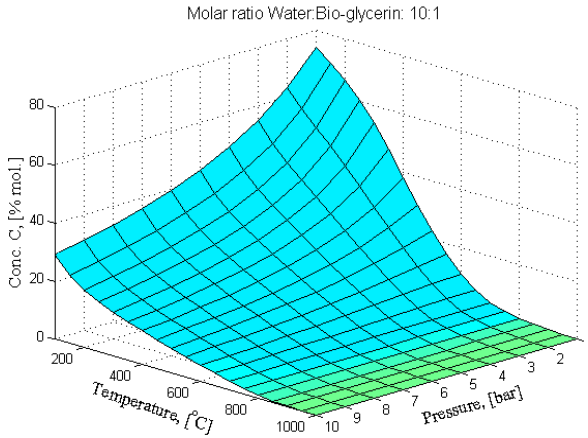
1. $C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$
2. $C_3H_8O_3 \leftrightarrow 4H_2 + 3CO$
3. $CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO$
4. $CO + H_2O \leftrightarrow H_2 + CO_2$
5. $CO + 3H2 \leftrightarrow CH4 + H2O$
6. $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$
7. $2CO \rightarrow CO_2 + C$
8. $CH_4 \rightarrow 2H_2 + C$
9. $CO + H_2 \rightarrow H_2O + C$
10. $CO_2 + 2H_2 \rightarrow 2H_2O + C$

Zsolt Tasnadi-Asztalos,[a]* Arpad Imre-Lucaci,[a] Calin-Cristian Cormos,[a]Ana-Maria Cormos,[a] Mihaela-Diana Lazar,[b] Paul-Serban Agachi[a], **Thermodynamic Study of Hydrogen Production via Bioglycerol Steam Reforming,** Proceedings of the 24th European Symposium on Computer Aided Process Engineering – ESCAPE 24 June 15-18, 2014

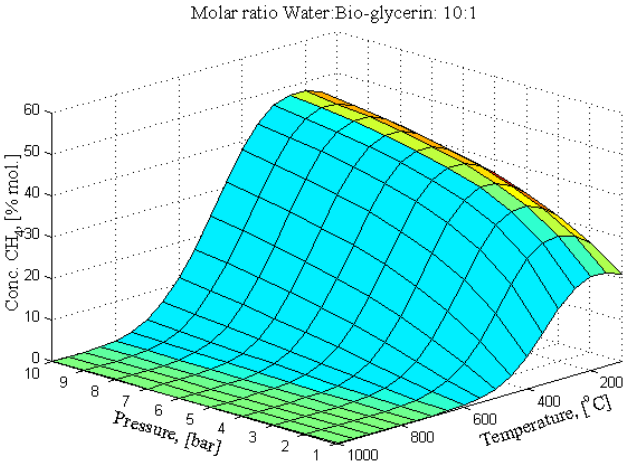
# Results of thermodynamic study via bioglycerol steam reforming



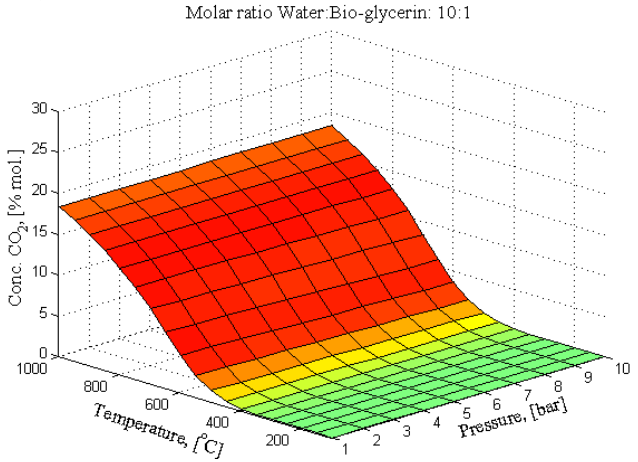

a) Variation of $H_2$ concentration with temperature and pressure




b) Variation of C concentration with temperature and pressure




c) Variation of $CH_4$ concentration with temperature and pressure




d) Variation of $CO_2$ concentration with temperature and pressure

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# In progres

## Kinetic modeling of bioglycerol catalytic steam reforming

## Analysis of different types of concepts of 100MW thermal power production from bioglycerol

- Bioglycerol autothermal reforming
- Bioglycerol steam reforming
- Chemical looping

# In future plan

Analysis of different types of concepts of 100MW thermal power production from bioethanol

Dynamic simulation of hydrogen production from bioglycerol steam reforming in continuous tubular reactor

# Dissemination of results

- Zsolt Tasnadi-Asztalos, Ana-Maria Cormos, Árpád Imre-Lucaci, and Clin C. Cormos, **Thermodynamic Evaluation of Hydrogen Production via Bioethanol Steam Reforming,** AIP Conference Proceedings **1565**, 175 (2013)
- **Zsolt Tasnádi-Asztalos[a], Árpád Imre-Lucaci[a], Ana-Maria Cormoş[a], Mihaela Diana Lazăr[b], Paul-Șerban Agachi[a], Thermodynamic Study and Kinetic Modeling of Bioethanol Steam Reforming,** Studia UBB Chemia, LVIII, 4, 2013
- Zsolt Tasnadi-Asztalos,[a]* Arpad Imre-Lucaci,[a] Calin-Cristian Cormos,[a]Ana-Maria Cormos,[a] Mihaela-Diana Lazar,[b] Paul-Serban Agachi[a], **Thermodynamic Study of Hydrogen Production via Bioglycerol Steam Reforming,** Proceedings of the 24th European Symposium on Computer Aided Process Engineering – ESCAPE 24 June 15-18, 2014