

Mathematical modelling of kinetics of bio-methanol production on fibrous Cu/Zn/Al/Zr catalyst from biomass derived syngas

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INTRODUCTION & AIM

Background

The accelerated expansion of global economy has contributed to the shift towards sustainable energy sources for bio-methanol production from renewable biomass. Methanol has attracted attention as it is crucial commodity in the present and future chemical and energy industries due to its various application (Cherubini, 2011).

Main Objective

The main objective is to develop a kinetic model for methanol synthesis on fibrous Cu/Zn/Al/Zr catalysts, integrating reaction kinetics, equilibrium constraints, and catalyst morphology

Specific Objectives

- I. To formulate rate equations based on Graaf's dual-site Langmuir-Hinshelwood kinetics for, CO hydrogenation, CO₂ hydrogenation and Reverse water gas shift (RWGS)
- II. To incorporate equilibrium constraints using thermodynamic data.
- III. To simulate the reactor in MATLAB (ODE solvers)
- IV. To validate the model against experimental data from literature/pilot studies.

METHOD

Kinetic Modelling

The rate expressions for methanol synthesis are derived from the Graaf's dual-site Langmuir-Hinshelwood kinetic model on the fibrous Cu/Zn/Al/Zr catalyst. This considers the three main reactions such as CO and CO₂ hydrogenation as well as the Reverse Water Gas shift. These expressions are mainly functions of partial pressure of reactants and products, rate constant and adsorption equilibrium constants.

CO hydrogenation: $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$

CO₂ hydrogenation: $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$

Reverse water gas shift (RWGS): $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$

(Eq1)

(Eq2)

(Eq3)

Key Variables

Table 1: Table of variables studied and optimal ranges

Variable	Optimal Range studied
Reaction Temperature	483-543K
Reaction Pressure	10-20MPa
Space Velocity	1000-10 000 (ml.g ⁻¹ .h ⁻¹)
Syngas Composition	3:1 molar ratio
Catalyst Mass (W)	0-10kg

Table 2: The regressed parameters mentioned in the table below are obtained from the Xin et al., (2009).

Parameters	A	B or -E
KCO	8.3965×10^{-11}	1.1827×10^5
KCO ₂	1.7214×10^{-10}	8.1287×10^4
$\text{KH}_2\text{O} / \text{KH}_2^{1/2}$	4.3676×10^{-12}	1.1508×10^5
K ₁	4.0638×10^{11}	-1.1695×10^4
K ₂	9.0421×10^8	-1.1286×10^5
K ₃	1.5188×10^{-33}	-2.6601×10^5

Model Formulation

The MATLAB ordinary differential equations (ODE 15) solver was used to calculate the mass balances of each chemical species (CO, CO₂, H₂, CH₃OH and H₂O) in a fixed bed reactor.

RESULTS & DISCUSSION

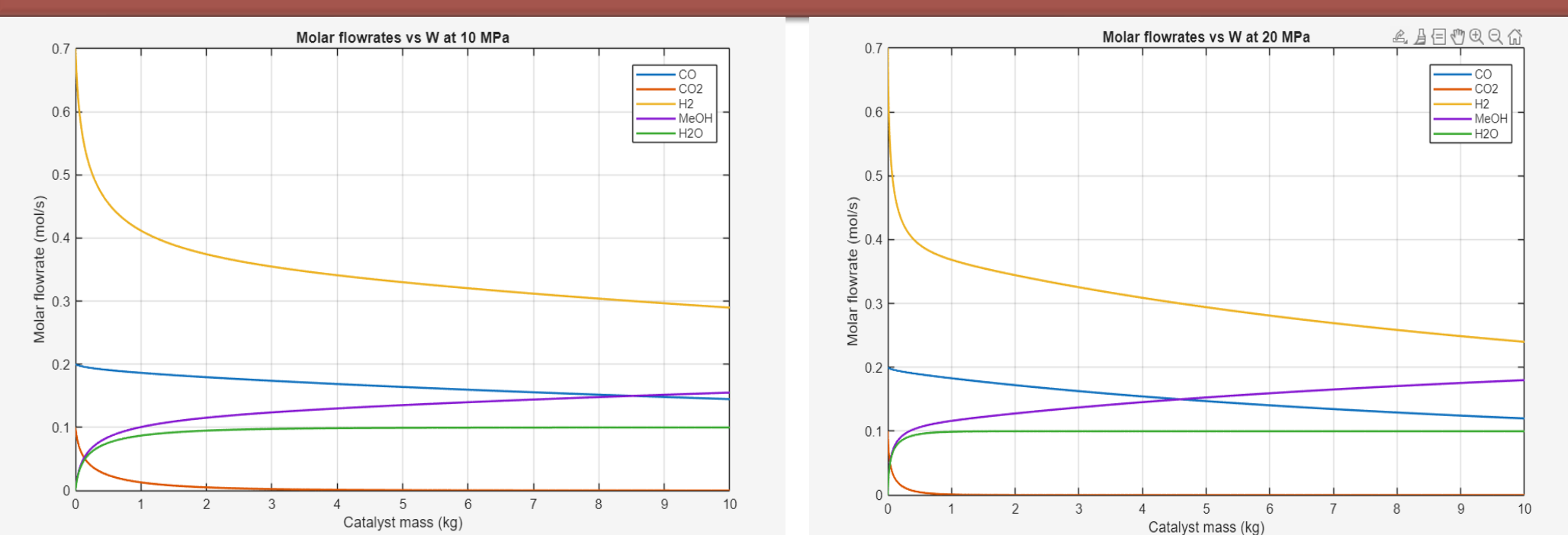


Figure 1: Molar Flowrates vs Catalyst Mass (P=10.0 MPa) and Molar flowrates vs Catalyst Mass (20.0 MPa).

Conversion of CO and CO₂ vs Catalyst Mass at varying pressures

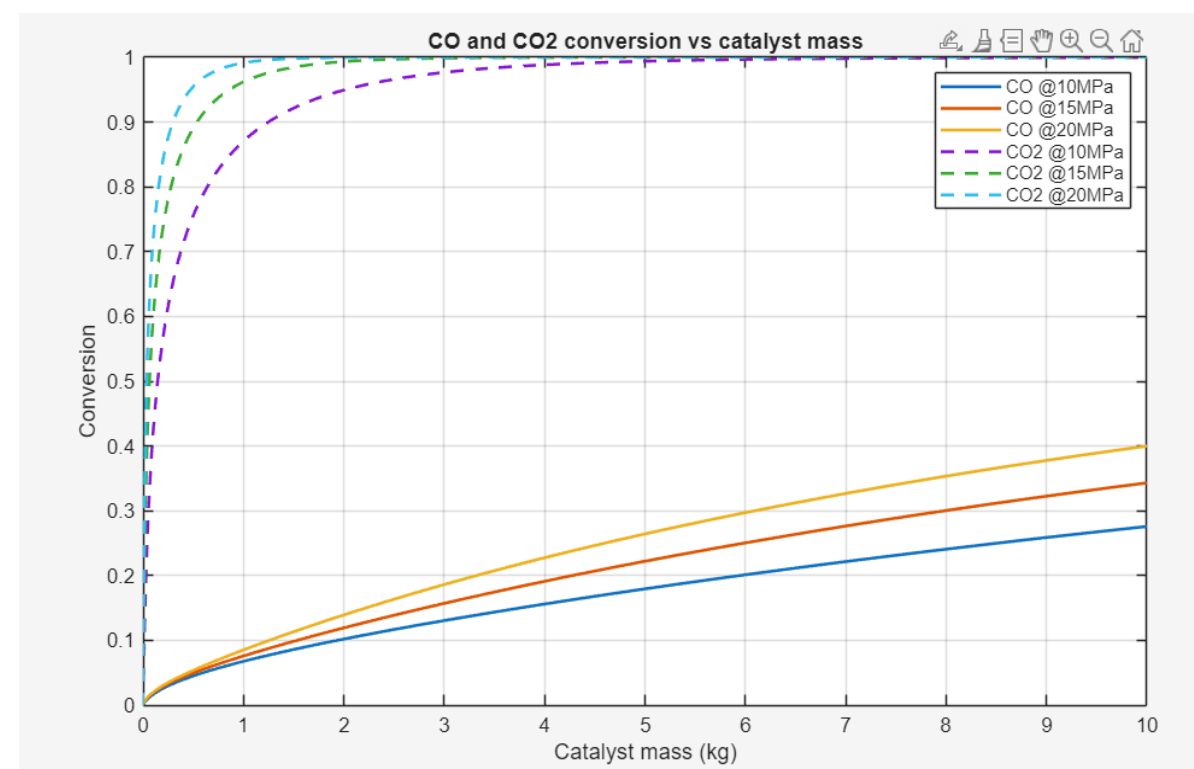


Figure 2: The graph of CO₂ conversion vs catalyst Mass (P=10.0, 15.0 and 20.0MPa).

Statistical analysis and model fitness

Model Validation

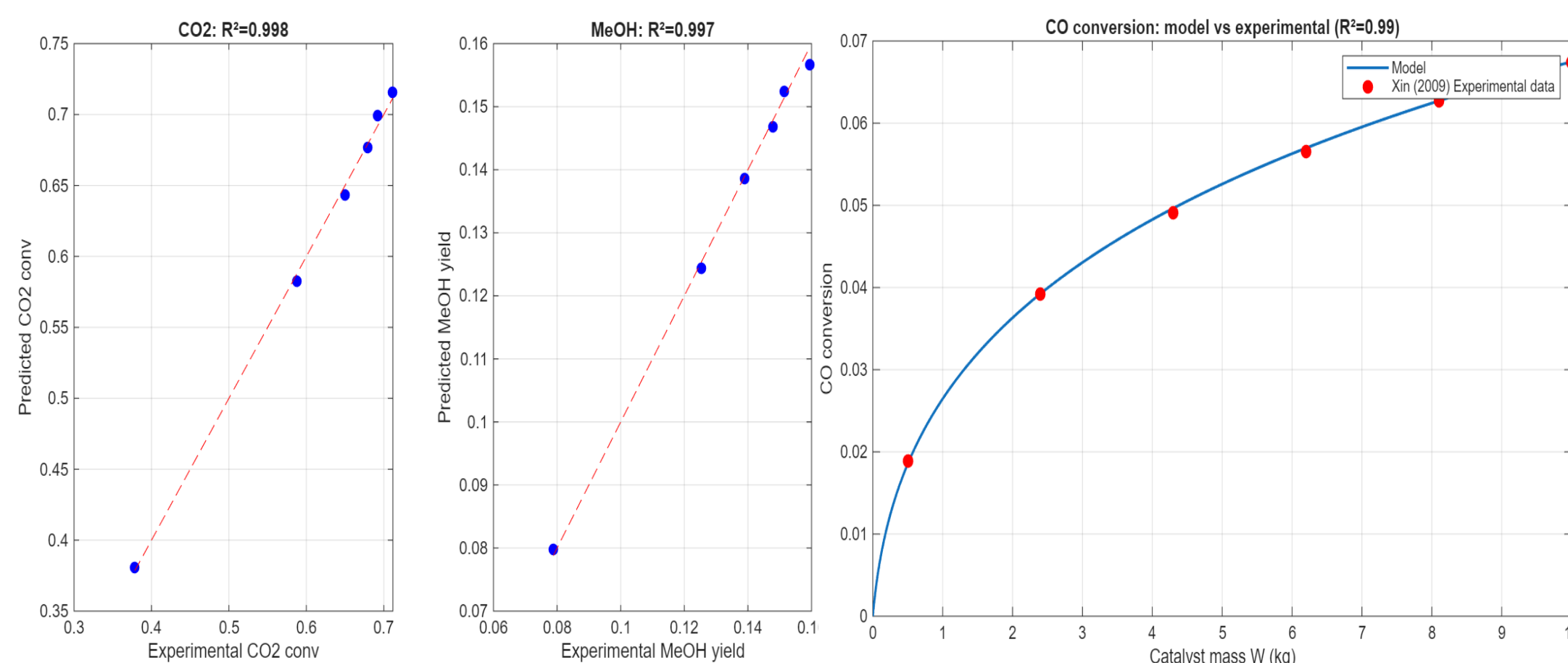


Figure 3: Distribution of experimental and simulated methanol data, Error analysis and Residual Distribution.

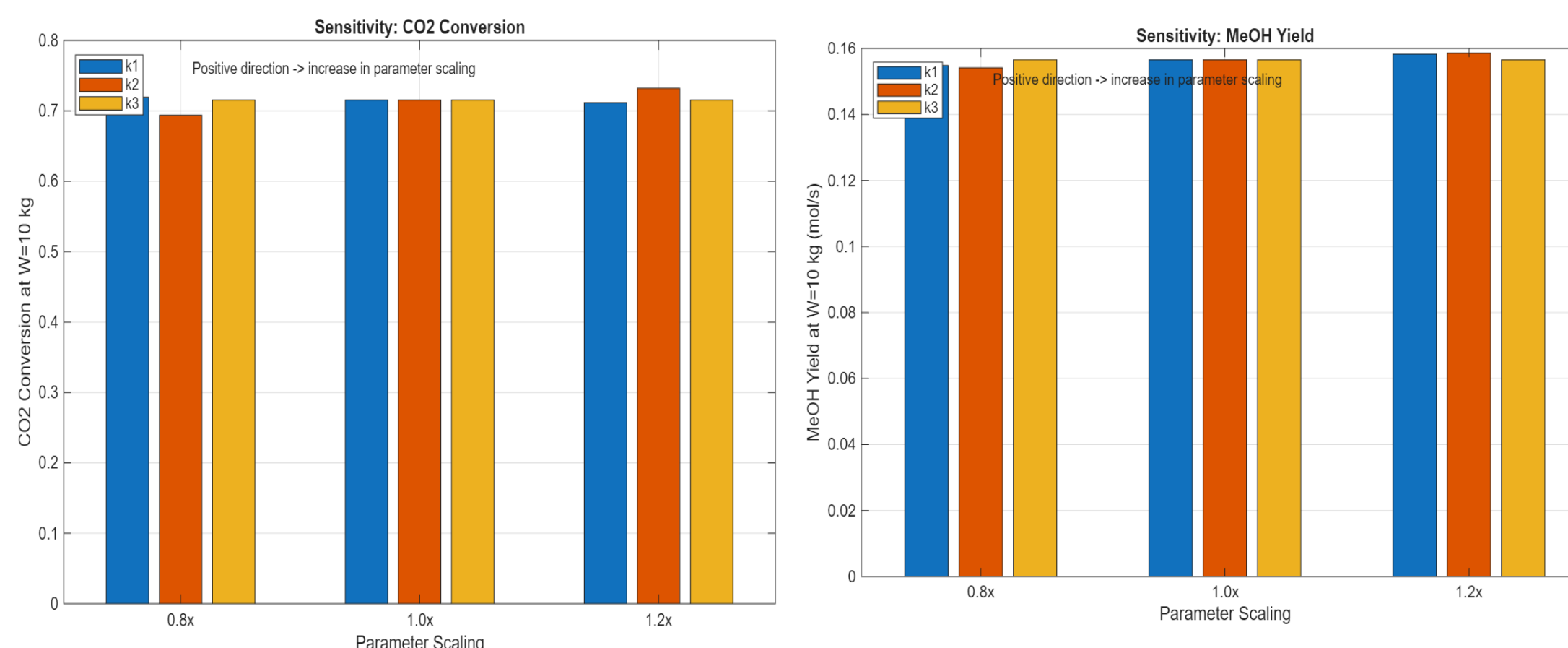


Figure 4: Global ranking of kinetic parameter based on sensitivity index for CO₂ conversion methanol yield.

CONCLUSION

- The comprehensive kinetic model for methanol synthesis on fibrous catalyst was successfully developed.
- The kinetic model effectively simulated the methanol yield as well as the CO₂ conversion under operating condition, demonstrated good agreement with experimental data from Xin et al, 2009.
- The results obtained confirmed the importance of pressure, which positively influence methanol production.

FUTURE WORK / REFERENCES

Future work: further optimization of catalyst to enhance CO₂ activation and reduce competing reverse water gas shift activity, while limiting carbon efficiency across all studied conditions is highly recommended.

Cherubini, F; Strømman, A.H. (2011). Life cycle assessment of bioenergy systems: state of the art and future challenges. Bioresource Technology, 102 (2011) 437–451