PURDUE UNIVERSITY

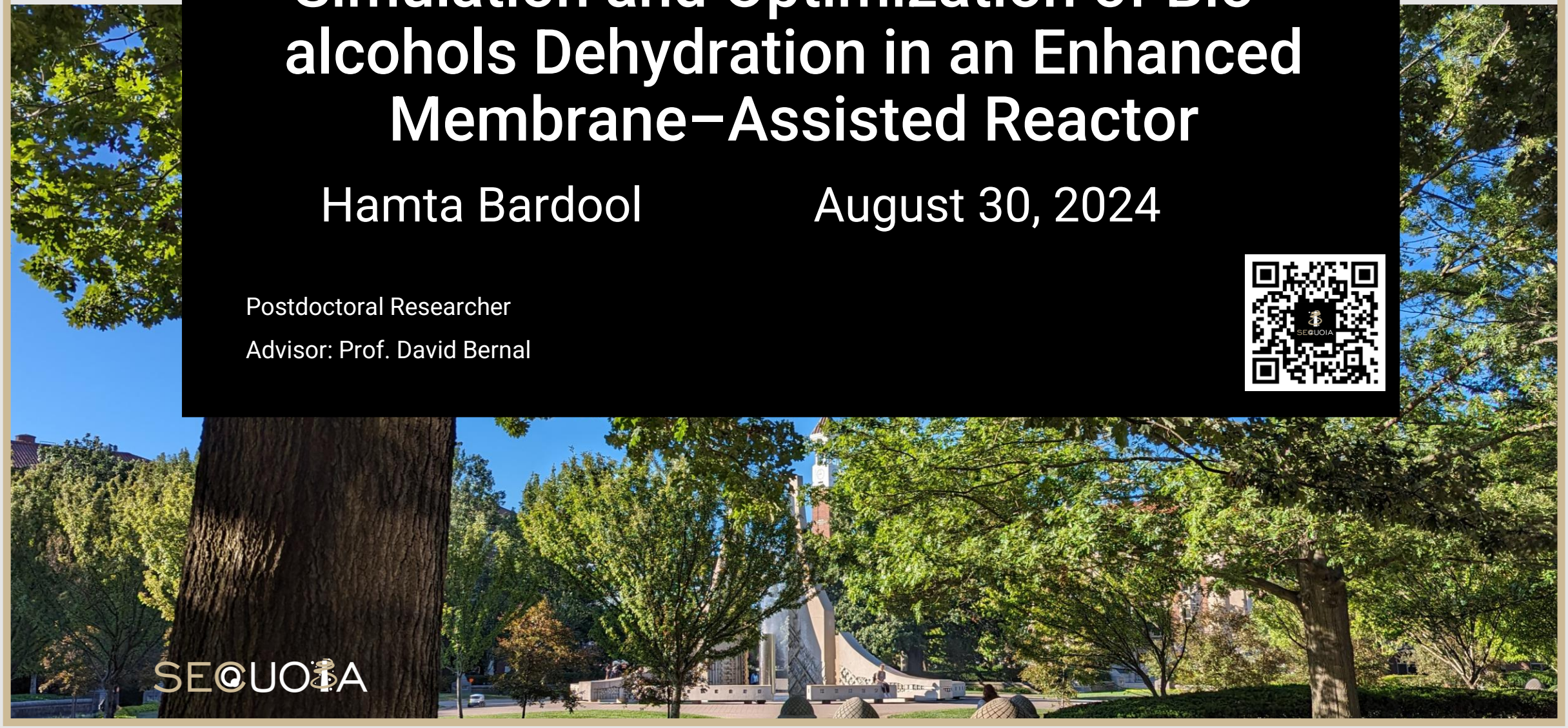
Simulation and Optimization of Bio–alcohols Dehydration in an Enhanced Membrane–Assisted Reactor

Hamta Bardool

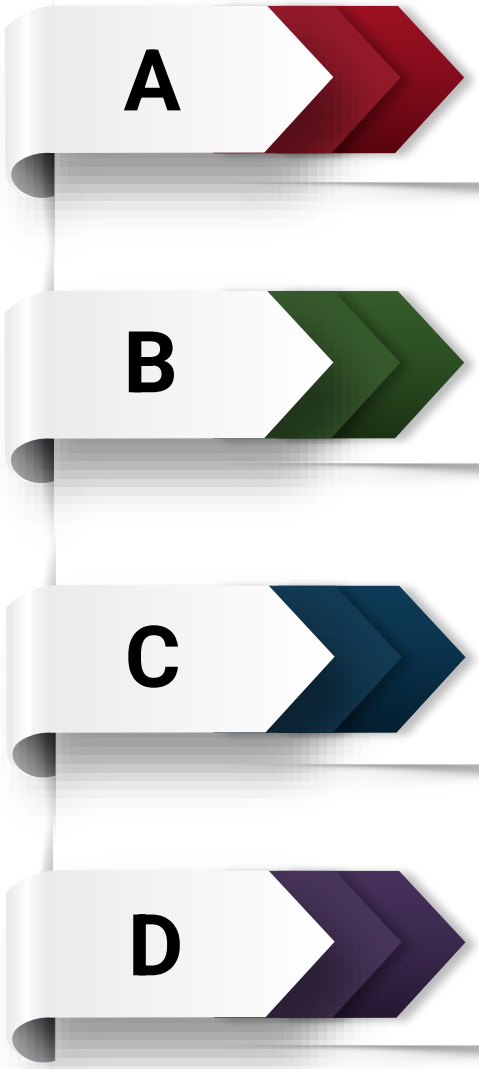
August 30, 2024

Postdoctoral Researcher

Advisor: Prof. David Bernal



Overview



Introduction

- Converting bio–mass to bio–fuel
- Bio–fuel (DME and DEE)
- Bio–alcohol dehydration

The Objective of this Project

Model Description

- Membrane–assisted bio–alcohol dehydration reactor
- Governing equations
- Kinetics of bio–alcohol dehydration
- Numerical solution

Results and Discussion

- Model validation
- Optimized M–BMDR
- Optimized M–BEDR

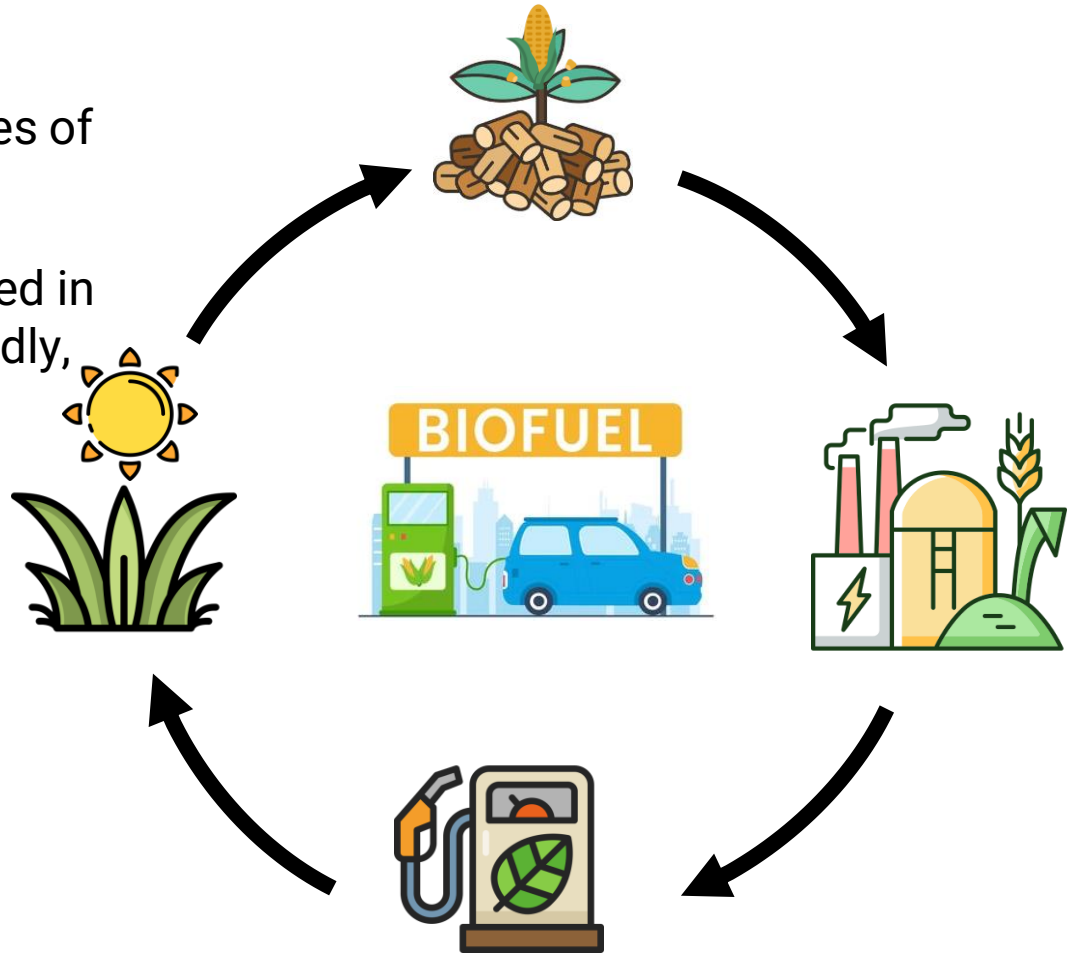
Introduction

Converting biomass to biofuels and chemicals has the advantages of **sustainability** and **renewability**.[1,2]

Biofuels, which can be solid, liquid, or gas, have been widely utilized in transportation because they are clean, safe, environmentally friendly, and sustainable sources.

Converting biomass into valuable products such as fuels and olefins makes it a potential alternative to fossil fuels.

Converting bio–alcohols, which are produced from biomass sources, is currently a major trend.

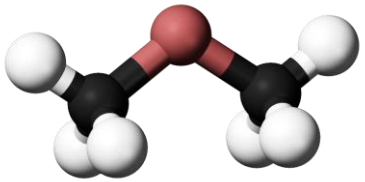


1. K. Kucharska et al., Renewable Energy 129 (2018) 2. Anu et al., Renewable Energy 160 (2020).

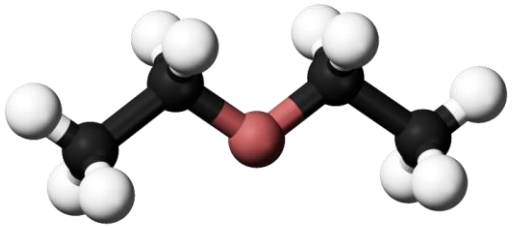
Introduction

Biofuel[1,2]

Produced from bio–methanol



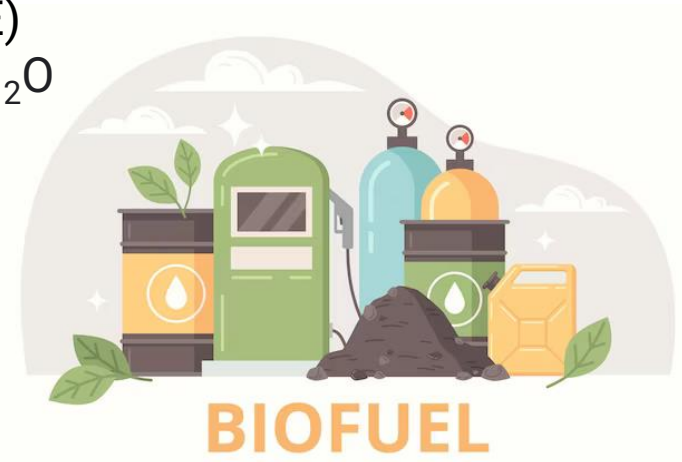
Dimethyl ether (DME)
C_2H_6O



Diethyl ether (DEE)
$(C_2H_5)_2O$

Produced from bio–ethanol

- Utilized instead of diesel fuel and liquefied petroleum gas (LPG)[3,4]
- Higher cetane number compared to diesel fuel[5,6]
- Low greenhouse gas emissions[5,6]



1. B. Mohan et al., Applied Energy 185 (2017), 2. K.C. Tokay et al., Chemical Engineering Journal 184 (2012), 3. A.R. Zahedi, S.A. Mirnezami, Renewable Energy 162 (2020), 4. S.H. Park, C.S. Lee, Energy Conversion and Management 86 (2014), 5. G. Thomas et al., Fuel Processing Technology 119 (2014), 6. M. Senthil Kumar et al. J. Eng. Gas Turbines Power (2010)

Introduction

Bio–Alcohol Dehydration

Bio– MeOH Dehydration[1,2]

Exothermic Reaction

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$$

Acidic Catalyst

Bio–EtOH Dehydration[3]

Endothermic Reaction

$$C_2H_5OH \xrightarrow{k_1} C_2H_4 + H_2O$$

$$2C_2H_5OH \xrightarrow{k_2} (C_2H_5)_2O + H_2O$$

$$(C_2H_5)_2O \xrightarrow{k_3} 2C_2H_4 + H_2O$$

$$C_2H_5OH \xrightarrow{k_4} C_2H_4O + H_2$$

$$2C_2H_4 \xrightarrow{k_5} C_4H_8$$

Bio–alcohols contain considerable quantities of water

Membrane–assisted processes can enhance the performance of the reactor in terms of conversion and product purity.

1. Z. Bai et al., Polish Journal of Chemical Technology 15.2 (2013), 2. M. Alavi et al. Science and Technology 3.2 (2013), 3. A.P. Kagyrmanova et al., Chemical Engineering Journal 176–177 (2011)

Introduction

Bio–Alcohol Dehydration

Bi

Ex

$2CH_$

Bio–alcoho
water

The Objective of this Project

Investigating the feasibility of bio–alcohol dehydration using a membrane-assisted reactor, optimizing conditions for better conversion and products purity

Membrane–assisted processes can enhance the performance of the reactor in terms of conversion and product purity.

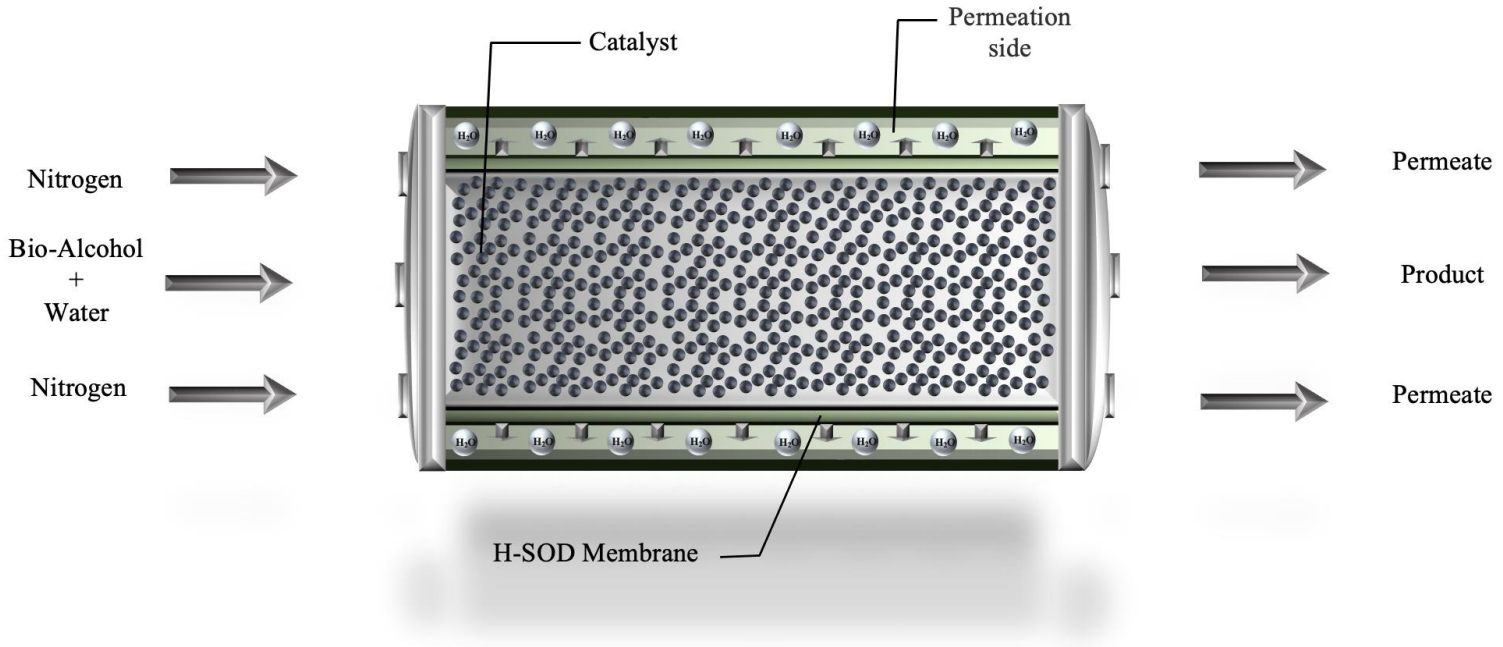
$$C_2H_5OH \rightarrow C_2H_4O + H_2$$

$$2C_2H_4 \xrightarrow{k_5} C_4H_8$$

1. Z. Bai et al., Polish Journal of Chemical Technology 15.2 (2013), 2. M. Alavi et al. Science and Technology 3.2 (2013), 3. A.P. Kagyrmanova et al., Chemical Engineering Journal 176–177 (2011)

Model Description

- The reactor of bio–alcohol dehydration includes a fixed bed and the surrounding perm-selective membrane.



- To investigate the effect of various variables on the bio–alcohol dehydration process and determine the optimal operating conditions, the M–BMDR and M–BEDR systems are modeled using a mathematical model including the conservation of **mass, energy, and momentum** in both reaction and membrane zones.

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Model Description

- **Assumptions for deriving a mathematical model and evaluating the enhanced M–BMDR and M–BEDR performance.**

  - Steady–state condition is applied in both reaction and membrane zones.
  - The radial gradient is ignored in both reaction and membrane zones.
  - High gas velocity makes the dispersion effects negligible.
  - Porosity is constant in the reaction zone.
  - Non–ideal reacting mixtures
  - No lateral heat loss in the system (adiabatic operation).
  - Homogeneous reactions are considered (i.e., gas–phase reactions).
  - The Ergun equation is considered for the pressure drop.
  - No pressure drop on the membrane side
  - The H–SOD membrane is only water permeable.

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Model Description

- Governing equations of the membrane–assisted bio–alcohol dehydration reactor: [1,2]

1 Mass Balance

Reaction Side:

$$\frac{-1}{A_c}\frac{dF_i}{dz} + \eta\rho_B r_i - \beta\frac{\pi D}{A_c}J_{H_2O} = 0; \quad \beta = 1\ for\ H_2O\ else\ \beta = 0$$

Permeation Side:

$$-\frac{dF_i}{dz} + \varphi\pi D_m J_{H_2O} = 0; \quad \varphi = 1\ for\ H_2O\ else\ \varphi = 0 \qquad J_{H_2O} = \frac{Q_{H_2O}A_s}{V_r}\left(P_{H_2O} - P_{H_2O,m}\right)$$

Input - Output + Generation - Consumption = Accumulation

$$F_A(z) - F_A(z+dz) - \eta\rho_B r_A(z)\, A_c\, \mathrm{dz} = 0$$

Divided by dz and take the limit as it approaches zero

$$\frac{dF_A}{dz} = -\eta\rho_B r_A(z)\, A_c$$

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021), 2. A. Bakhtyari et al., Journal of Natural Gas Science and Engineering 26 (2015),

Model Description

- Governing equations of the membrane–assisted bio–alcohol dehydration reactor: [1,2]

2 Energy Balance

Reaction Side:

$$\frac{-C_p^g}{A_c}\frac{d(F_t T)}{dz} + \rho_B \sum_{i=1}^{Nc} r_i(-\Delta H_{f,i}) - \frac{\pi D}{A_c} U\left(T - T_p\right) - J_{H_2O}(T - T_p) = 0$$

Permeation Side:

$$-C_{p,m}^g \frac{d\left(F_{t,p} T_p\right)}{dz} + \pi D_m J_{H_2O} \int_{T_p}^{T} C_{p,H_2O}^g dT + \pi D U\left(T - T_p\right) = 0$$

Energy In − Energy Out + Energy Generation − Energy Consumption = Accumulation

$$\frac{-C_p^g}{A_c}\frac{d(F_t T)}{dz} + \rho_B \sum_{i=1}^{Nc} r_i(-\Delta H_{f,i}) - \mathrm{q(z)} = 0$$

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021), 2. A. Bakhtyari et al., Journal of Natural Gas Science and Engineering 26 (2015),

Model Description

- Governing equations of the membrane-assisted bio–alcohol dehydration reactor: [1,2]

3 Pressure Drop

Pressure drop (Reaction side):

$$\frac{dP}{dz} = \frac{150\mu}{\phi_s^2 dp^2}\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{Q}{A_c} + \frac{1.75\rho}{\phi_s d_p}\frac{(1-\varepsilon)}{\varepsilon^3}\frac{Q^2}{A_c^2}$$

4 Boundary condition

Reaction side:

$$z = 0 \implies F_i = F_{i,0};\ T = T_0;\ P = P_0;$$

Permeation Side:

$$z = 0 \implies F_i = F_{i,0};\ T_P = T_{P,0};$$

5 Heat transfer coefficient

Reaction sides:[3]

$$h = \frac{\gamma k_{th}(1-\varepsilon)}{\varepsilon d_p} Re^{\acute{}1/2} Pr^{1/3}$$

Membrane sides:[4]

$$h = 0.0214\frac{k_{th}}{D} Pr^{0.4}\left(Re_D^{0.8} - 100\right)$$

Overall:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{A_i \ln(D_0/D_i)}{2\pi z k_w} + \frac{A_i}{A_o}\frac{1}{h_o}$$

1. S. Khajavi et al., Catalysis Today 156 (2010), 2. A. Bakhtyari et al., Journal of Natural Gas Science and Engineering 26 (2015), 3. D. Thoenes Jr, H. Kramers, *Chemical Engineering Science* 8.3-4 (1958), 4. JP. Holman, JH. Boggs, (1960)

Model Description

- **Kinetics of bio–MeOH Dehydration[1,2]**

$$r_{MeOH} = k f_{MeOH}^2 \left(1 - \frac{f_{DME} f_{H_2O}}{K_{eq} f_{MeOH}^2}\right) \qquad k = 1457.024 \exp\left(-\frac{78072.55}{RT}\right)$$

$$\ln K_{eq} = -26.64 + 3.707 \ln T + \frac{4019}{T} - 2.783 \times 10^{-3} T + 3.8 \times 10^{-7} T^2 + 6.561 \times \frac{10^4}{T^3}$$

- **Kinetics of bio–EtOH Dehydration[3]**

Ethylene (c_2) formation from EtOH: $r_{c_2} = k_1 f_{EtOH}$

DEE formation from EtOH: $r_{DEE} = k_2 f_{EtOH}^2$

Ethylene (c_2) formation from DEE: $r_{c_2} = k_3 f_{DEE}$

Acetaldehyde (AA) formation from EtOH: $r_{AA} = k_4 f_{EtOH}$

Butylene (c_4) formation from ethylene (c_2): $r_{c_4} = k_5 f_{c_2}^2$

- **Peng–Robinson equation of state (PR EoS) was utilized to calculate the fugacity of each component.**

1. Z. Bai et al., Polish Journal of Chemical Technology 15.2 (2013), 2. M. Alavi et al. Science and Technology 3.2 (2013), 3. A.P. Kagyrmanova et al., Chemical Engineering Journal 176–177 (2011)

Model Description

Numerical Solution

The **finite difference method** is utilized to convert the set of ODE equations to nonlinear algebraic equations.

The reactor length is divided into 200 separated sections to assure negligible numerical error.

Multi–Objective Optimization

The main goal of optimization → Best performance of the system → Multi–objective optimization of the M–BMDR and M–BEDR (Evolutionary Algorithms)

$$X_i = \frac{F_{i,in} - F_{i,out}}{F_{i,in}} \times 100 \qquad i = MeOH\ or\ EtOH$$

$$Y_{DME} = \frac{F_{DME,Out}}{F_{MeOH,in}} \times 100$$

$$Y_i = \frac{F_{i,Out}}{F_{EtOH,in}} \times 100 \qquad i = DEE, Ethylene, or\ Butylene$$

Maximize the bio–alcohol conversion and the production yield of the desired compounds .

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Results and Discussion

Model Validation

The results of an adiabatic MeOH dehydration reactor[1] were collected and compared against the results of the mathematical model.

Input feed stream= 1558.28 mol/s

Industrial reactor= 4 m in diameter and 8.08 m in length

Feed= 93 mol.% MeOH, 6 mol.% DME, and 1 mol.% water

T= 533 K

P=18.2 bar

ρ_C=2010 kg/m^3

bed void fraction= 50%

Comparing model predictions with the real plant data of the conventional MeOH dehydration reactor

Output variable	Real plant data	Model prediction	Error (%) [a]
Temperature (K)	644	659	2.3
MeOH flowrate (kmol/hr)	937	930	0.7
DME flowrate (kmol/hr)	2506	2480	1.0

a: $\mathbf{Error} = \left|\frac{x_{Real} - x_{Model}}{x_{Real}}\right| \times 100$

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Results and Discussion

Optimized M–BMDR

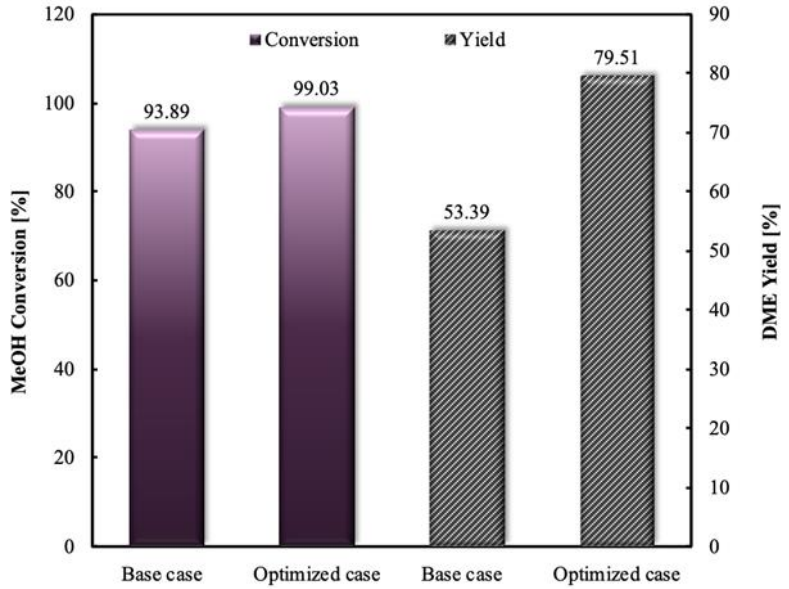
The results of the system in the optimum condition is compared with the base case in this section.

The comparison is based on **reaction–side temperature profile**, **MeOH conversion**, and **DME yield**.

The main objective of the optimization: **Maximizing MeOH conversion as well as DME yield**

Optimized operating conditions of M–BMDR

Parameter	Value	
	Optimized case	Base case
Inlet pressure (bar)	21.86	18.2
Inlet temperature (K)	559	533
Sweep gas temperature (K)	433	413
Total feed flowrate (kmol/hr)	44.9	56.1
Sweep gas flowrate (kmol/hr)	52.1	72
Feed Composition (Molar fraction)		
MeOH	0.20	0.93
DME	0.06	0.06
Water	0.74	0.01



Comparing the axial profiles of output conversions and product yields in the base case and optimized case

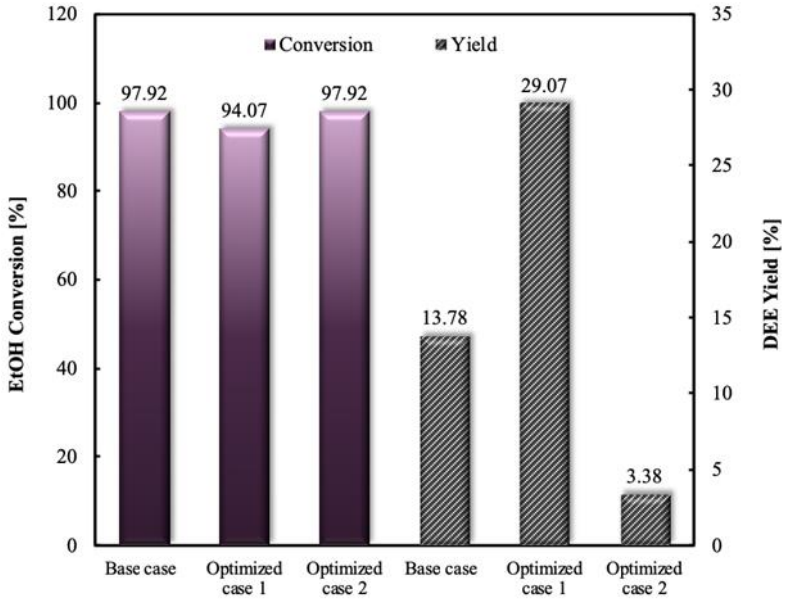
1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

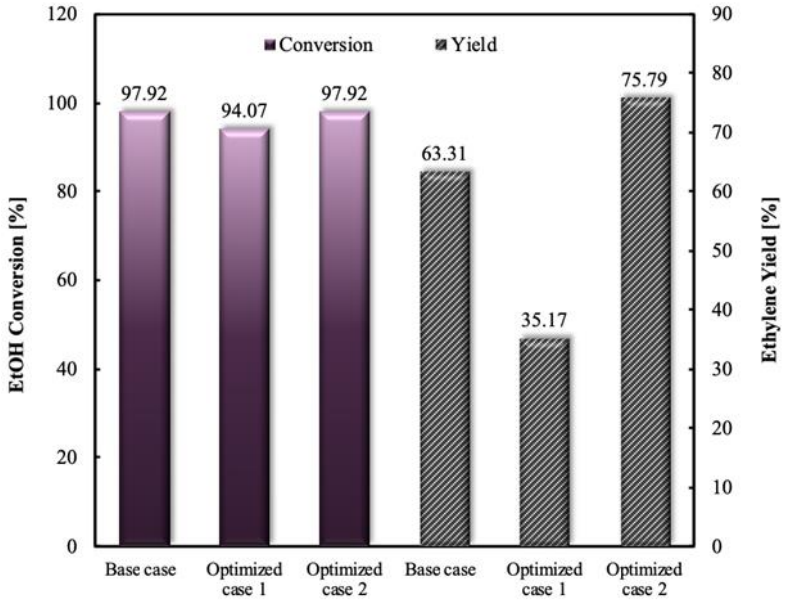
Results and Discussion

Optimized M–BEDR

The comparison is based on **reaction–side temperature profile**, **ETOH conversion**, and **Ethylene and DEE yield**.

The main objective of the optimization: **Maximizing EtOH conversion as well as Ethylene and DEE yield**





Optimized case 1:
Maximizing EtOH conversion as well as DEE yield

Optimized case 2:
Maximizing EtOH conversion as well as Ethylene yield

Comparing the axial profiles of output conversions and product yields in the base case and optimized case

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Results and Discussion

- **Optimized M–BEDR**

The comparison is based on **reaction–side temperature profile**, **ETOH conversion**, and **Ethylene and DEE yield**.

The main objective of the optimization: **Maximizing EtOH conversion as well as Ethylene and DEE yield**

Optimized operating conditions of M–BEDR

Parameter	Value		
	Optimized case 1	Optimized case 2	Base case
Inlet pressure (bar)	1.28	1.20	1.5
Inlet temperature (K)	666	695	700
Sweep gas temperature (K)	656	724	690
Total feed flowrate (kmol/hr)	6.7	4.5	5.61
Sweep gas flowrate (kmol/hr)	43.2	100.8	72.0
Feed Composition (Molar fraction)			
EtOH	0.96	0.96	0.96
Water	0.04	0.04	0.04

Optimized case 1: Maximizing EtOH conversion as well as DEE yield

Optimized case 2: Maximizing EtOH conversion as well as Ethylene yield

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Conclusion

The main achievement of this project is:

Extracting water during the reaction using a membrane reactor.

- **Optimized M–BMDR**

  - ↓ Feed flowrate and Methanol concentration
  - ↑ Temperature and Pressure

  → **Increase MeOH conversion and DME yield**

- **Optimized M–BEDR**

  - ↓ Temperature and Pressure

  → **Increase EtOH conversion, DEE yield, and Ethylene yield**

1. A. Bakhtyari, R. Bardool et al., Renewable Energy 177 (2021).

Future/Current work

Direct transcription

- NLP formulations
- Orthogonal collocation
- Pyomo.DAE

Challenges

- Different way of writing the code – Simulation to optimization formulation
- Degrees of freedom analysis
- Finding the best initialization

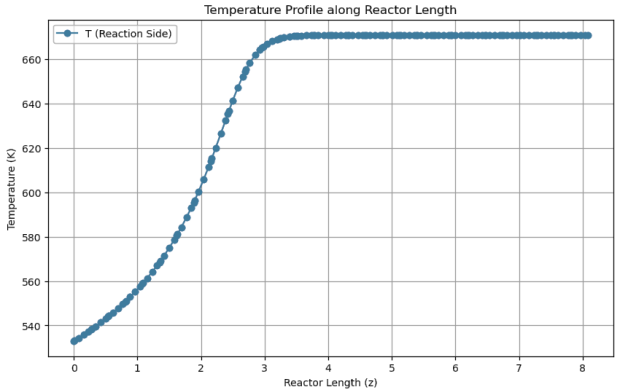
Future work

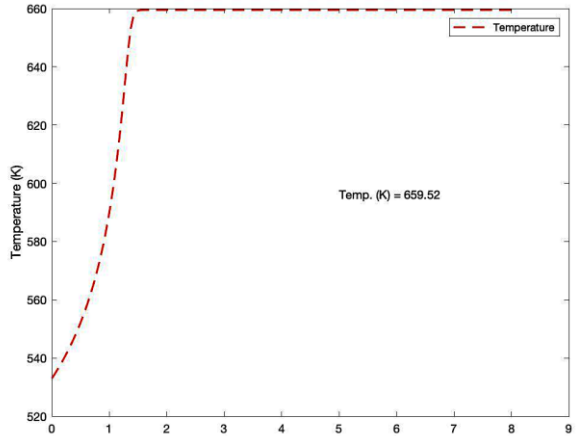
- Compare both approaches in terms of computational efficiency and the solution obtained.

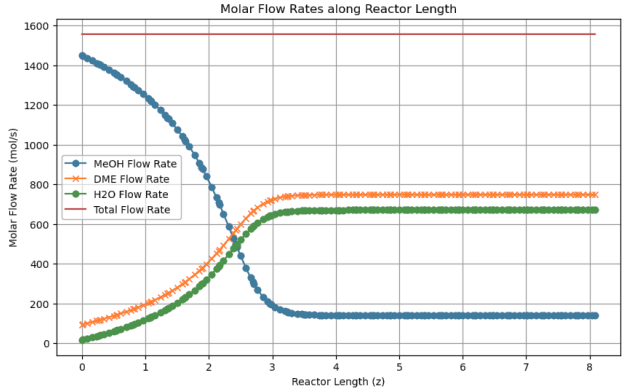
Future/Current work

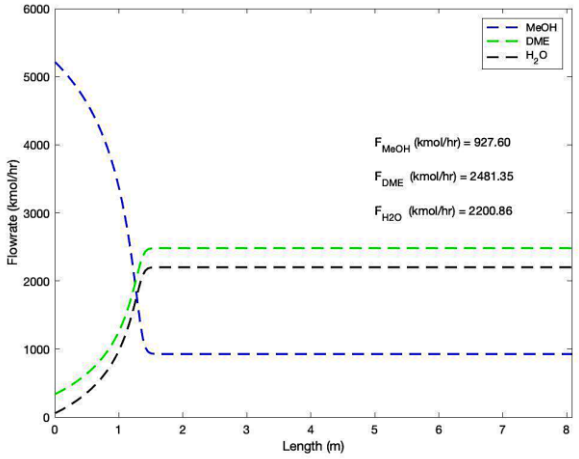
Future work

- Compare both approaches in terms of computational efficiency and the solution obtained.









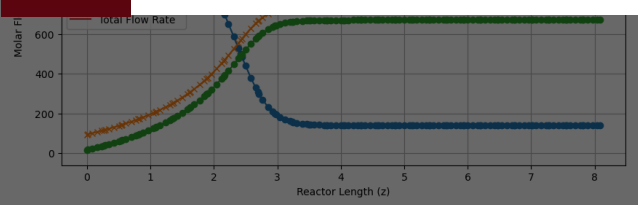
Future/Current work

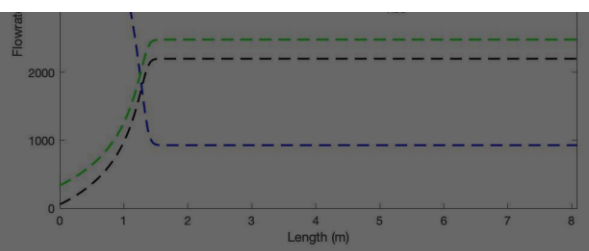
Future work

- Compare ... ed.

Conjecture

Combining the two will be the best: Initialize by integrating ODE and then solving the DAE optimally.





PURDUE UNIVERSITY

THANK YOU

FOR YOUR ATTENTION !