

Optimization of Liquid Phase Generation by Catalyzed Pyrolysis of PET Plastic Waste

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Abstract

Plastic waste that is not recycled causes significant environmental harm, making it essential to develop sustainable waste management and conversion strategies. Pyrolysis is a promising method for converting plastic waste into liquid fuel [1]. This research aims to enhance PET pyrolysis by evaluating the potential of a Nickel (II) Chloride (NiCl_2) catalyst toward a target 10% increase in liquid-phase production. A 2D axisymmetric model was developed using COMSOL Multiphysics® [2]. The results show that NiCl_2 and Al_2O_3 exhibit similar behavior, with less than 1% difference. Maximum concentrations reached approximately $8.0\text{E-}15 \text{ mol/m}^3$ at steady state. The validated parameters will be used in a 3D model to compare with experimental studies [3]. This study demonstrates the effectiveness of COMSOL Multiphysics in modeling catalytic pyrolysis processes and contributes to the optimization of chemical recycling of PET waste.

Keywords: Catalyst, Nickel (II) Chloride, Pyrolysis, Polyethylene Terephthalate (PET), HVP, LVP.

Introduction

Plastic waste presents a major environmental challenge due to its volume and slow degradation. Global plastic production reached 460 million tons in 2022, and waste has increased significantly over recent decades [4].

The United Nations reported that plastic pollution in marine environments could triple by 2040 [5].

In Puerto Rico, approximately 2.7 million tons of solid waste are generated annually, with plastics representing 13.9% of the waste stream [6]. PET waste has increased due to natural disasters and recent global events [7].

Theory / Experimental Set Up

Previous studies show that PET pyrolysis produces 23–40% liquid oil and 52–77% gas products [8]. Cepeliogullar and Putun (2013) reported liquid yields of 23.1% and noted high acidity in the produced oil [3]. The differences in yield are influenced by reactor type, temperature, and reaction time [8]. For example:

- Higher temperature → more cracking and acidity
- Reactor design affects heat distribution [3]

Catalysts such as Al_2O_3 have been widely used [3], while NiCl_2 has been recently studied for PET depolymerization with promising results [9].

Governing Equations / Numerical Model / Simulation / Methods / Use of Simulation Apps

Model Development

A COMSOL Multiphysics® simulation was performed using:

- A COMSOL 3D porous catalytic reactor model was selected as the reference reactor configuration because its geometry closely resembles the fixed-bed reactor reported by Cepeliogullar and Putun (2013). A simplified 2D axisymmetric model was then developed to validate the reaction and transport parameters under catalytic and non-catalytic conditions before their implementation in the 3D reactor model [3]

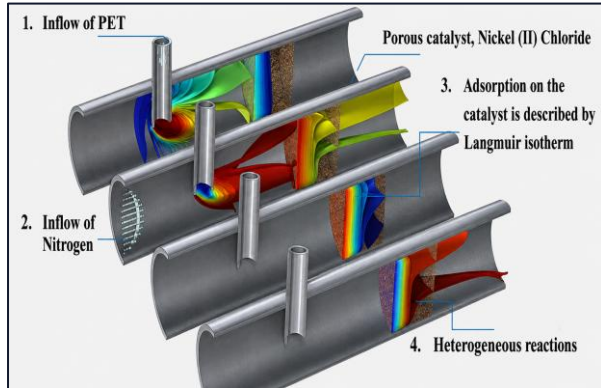


Figure 1. Porous Catalytic Reactor with Injection Needle model adapted to the parameters for the study of PET plastic waste and NiCl_2 catalyst (Multiphysics C. 6.1, 2023) [2]

- The 2D axisymmetric validation geometry is shown in Figure 2 [2]

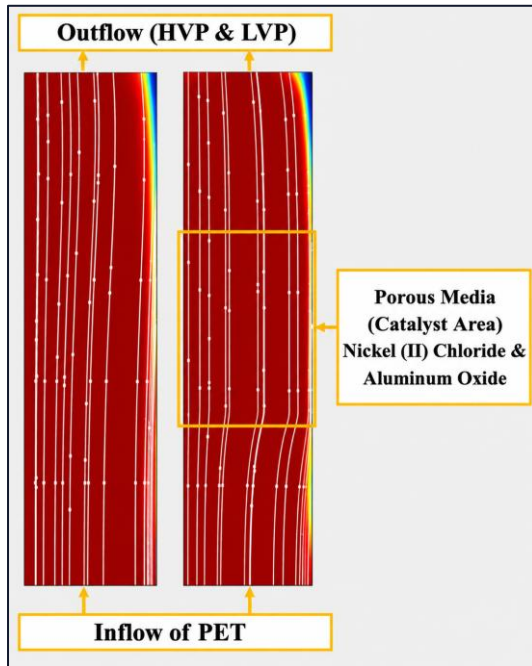


Figure 2. New 2D Axisymmetric Model without and with Catalyst

Three configurations were tested:

- No catalyst
- Al_2O_3 catalyst
- NiCl_2 catalyst

Governing Equations

The model incorporates reaction kinetics, species transport, surface reactions, and adsorption at the catalytic region. The 2D axisymmetric model was implemented in COMSOL Multiphysics® using the Chemical Reaction Engineering Module. The

model includes Laminar Flow, Brinkman Equations, Transport of Diluted Species in Porous Catalyst, and Chemistry physics interfaces. The Brinkman Equations and Transport of Diluted Species in Porous Catalyst interfaces are coupled through the Reacting Flow, Diluted species Multiphysics coupling to represent reactive species transport through the porous catalytic region. Reaction-rate coefficients are described using the Arrhenius expression [2]:

$$k_f = AT^\beta \exp\left(\frac{-E}{RT}\right)$$

Surface reactions are described using forward and reverse reaction-rate expressions as a function of surface coverage [2]. Species transport through the reactor is represented by the convection-diffusion-reaction balance.

$$u \cdot \nabla c_i = \nabla \cdot (D_i \nabla c_i) + R_i$$

The surface reaction rate, R_s , is expressed in terms of the respective surface coverage [2]:

$$R_s = k_f \theta_A \theta_B - k_r \theta_A \theta_B$$

Adsorption at the catalyst surface is represented using a Langmuir adsorption isotherm [2].

$$c_{P,i} = \frac{K_{L,i} c_{pmax,i} c_i}{1 + K_{L,i} c_i}$$

Assumptions

- PET decomposes into HVP ($\text{C}_7\text{H}_6\text{O}_2$) and LVP (C_2H_6) [3],[10]
- Kinetic parameters from Cepeliogullar and Putun (2013) [3]
- Catalyst loading of 5 wt% relative to PET was adopted based on Cepeliogullar and Putun (2013) [3]
- Constant operating parameters.

For this preliminary comparison, the same kinetic framework was applied to the non-catalytic, Al_2O_3 , and NiCl_2 cases. This assumption enables direct comparison but does not account for catalyst-specific reaction mechanisms or surface interactions. Therefore, the results represent a comparative modeling assessment rather than a complete description of catalyst-specific kinetics.

Experimental Results / Simulation Results / Discussion

The developed 2D axisymmetric model evaluates PET pyrolysis behavior under different catalytic conditions.

Key Findings

- Figure 3 shows without catalyst the model reached steady state at 65 s at velocity of 0.1 m/s. Both products exhibit slow reaction rates, with values nearing zero.

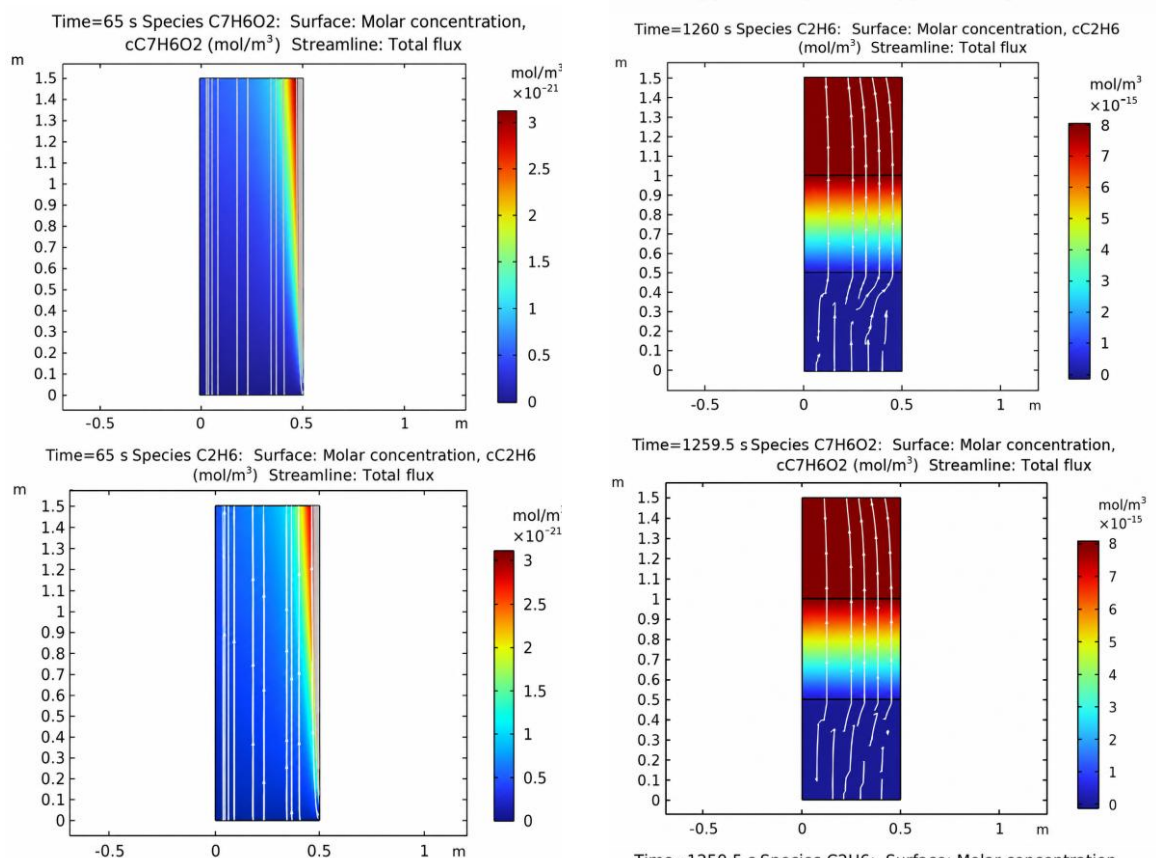


Figure 3. Test results without catalyst at 65 s (1.083 min): Products (HVP + LVP) are in a steady state

- Figure 4 shows with catalyst the model reached steady state at approximately 1260 s at velocity of 0.1 m/s. Both products exhibit slow reaction rates, with values nearing zero. NiCl_2 and Al_2O_3 behave similarly (<1% difference)

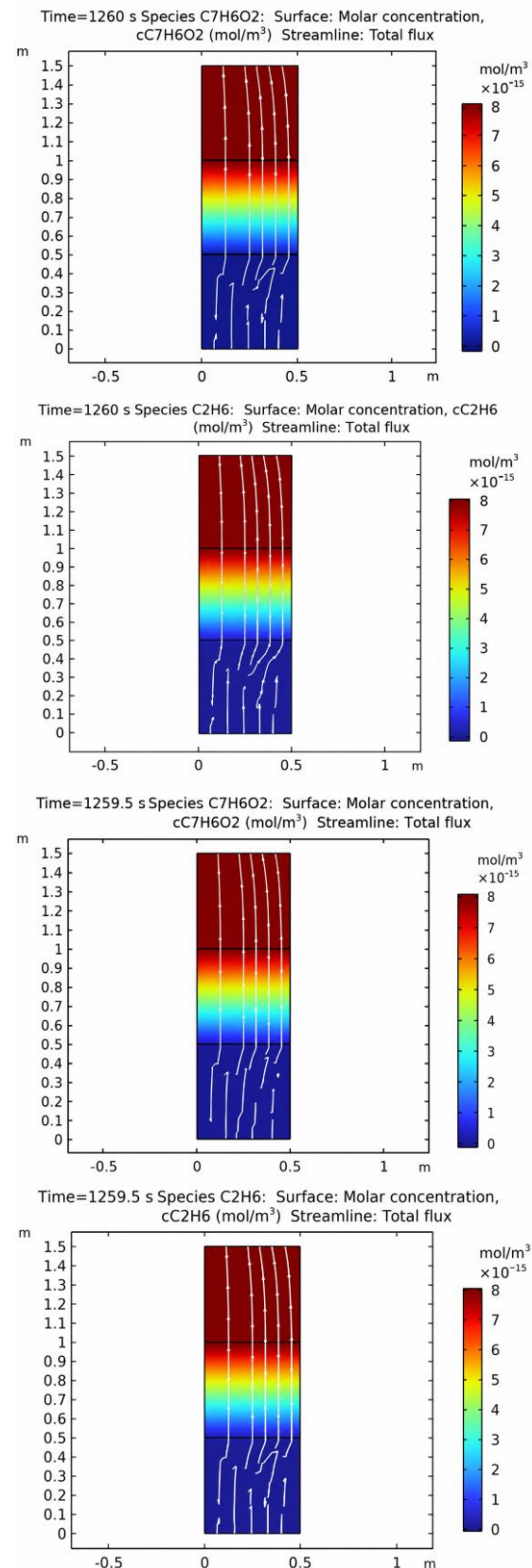


Figure 4. Test results with catalyst Al_2O_3 at 1260 s (21 min) & with catalyst NiCl_2 at 1259.5 s (20.99 min): Products (HVP + LVP) are in a steady state

Concentration Results

Maximum molar concentrations are shown in Figure 5:

- $\sim 8.0\text{E-}15 \text{ mol/m}^3$ with catalysts
- $\sim 10^{-21} \text{ mol/m}^3$ without catalyst

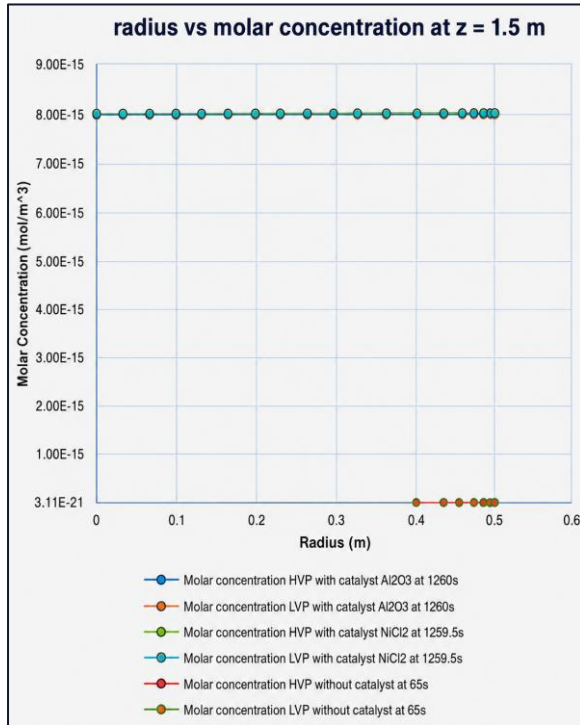


Figure 5. Molar concentration of HVP and LVP versus radius at $z = 1.5 \text{ m}$ for the non-catalytic, Al_2O_3 , and NiCl_2 cases.

Table 1: Effect of velocity (0.1 m/s to 0.2 m/s) and temperature (698K to 798K) on HVP and LVP molar concentration at $z = 1.5 \text{ m}$

Molar Concentration at $z = 1.5 \text{ m}$			
Velocity	Temperature	Molar concentration HVP & LVP (Al_2O_3 at 1260 s)	Molar concentration HVP & LVP (NiCl_2 at 1259.5 s)
0.1 m/s	698 K	8.0E-15	8.0E-15
0.2 m/s	698 K	4.0E-15	4.0E-15
0.1 m/s	798 K	1.4E-11	1.4E-11

Table 1 indicates that:

- Increasing temperature $\rightarrow$ increases concentration
- Increasing velocity $\rightarrow$ decreases concentration

Catalyst Comparison

- NiCl_2 produces slightly higher outlet cross-sectional average concentrations ($\sim 0.33\%$) than Al_2O_3 and reaches steady state marginally faster.
- These results align with previous catalytic pyrolysis findings reported in the literature [3], [8], [9].

Conclusions

Under the evaluated modeling assumptions, NiCl_2 and Al_2O_3 exhibited very similar predicted performance in PET pyrolysis.

Key conclusions:

- Catalytic cases produced substantially higher predicted HVP and LVP concentrations than the non-catalytic cases.
- Differences between catalysts are minimal ($<1\%$)
- Temperature and flow velocity strongly affect results
- Simplified modeling provides effective comparison

Future work will include:

- 3D reactor modeling
- Liquid phase yield evaluation
- Experimental validation.

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