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Considerations for scaling up the polyethylene terephthalate (PET) recycling using microwave heating technology

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1. Introduction

Polyethylene terephthalate (PET) is one of the most widely produced and consumed thermoplastic polymers globally, with applications spanning from textiles and high-strength fibres to photographic films and disposable beverage containers[1]. Recent statistics indicate that global production of PET resin exceeded 24 million tons and is expected to continue to increase, potentially reaching 1800 million tons by 2050 [2], [3].Thus, this work explores the scale-up considerations for PET recycling using microwave-assisted glycolysis, leveraging experimental results obtained from laboratory analysis to recover its monomeric constituent, bis(2-hydroxyethyl) terephthalate (BHET). BHET can be employed in the reverse reaction, leading to the repolymerization of PET through polycondensation, closing the material loop [4].

A comprehensive mapping of the experimental protocols was obtained to quantify material and energy inputs and outputs. This analysis is crucial for developing a techno-economic framework to assess the efficiency and scalability of implementing microwave heating at an industrial level. The insights gained from this study are expected to significantly inform future scale-up efforts, ensuring enhanced economic viability and environmental sustainability compared to conventional heating methods.

2. Experimental Methodology

In this study, we investigated the scalability of the microwave-assisted depolymerization of PET to obtain high-purity BHET monomer using zinc oxide (ZnO) as a catalyst, based on experimental data. The laboratory-scale process was designed to optimize reaction conditions while ensuring energy efficiency and product quality.

2.1 Experimental Setup

The microwave-assisted setup consists of an MW-assisted reactor (**Milestone SynthWAVE**) with a 1 L reaction cavity capacity, as shown in Figure 1. The reactor is composed of a cylindrical Teflon vessel and can deliver a maximum microwave input power of 1500 W. The system allows agitation of the reaction medium using a magnetically driven stirrer and operates under maximum conditions of 300 ºC and 199 bar.

Additionally, the reactor is connected to a chiller, which refrigerates the magnetrons, keeping them below 45 ºC throughout the experiments. Heating rates can be adjusted, and the reaction progress can be monitored in real-time via a PLC screen, enabling better control of the process.

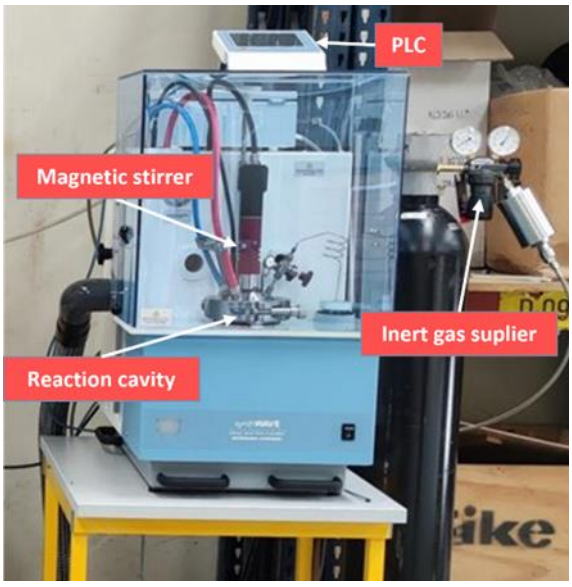

Figure 1. MW-assisted reactor (Milestone SynthWAVE)

2.2 Materials

a) Virgin polyethylene terephthalate (vPET)

The study was conducted on samples of virgin polyethylene terephthalate (vPET), with dimensions of 4x3x2 mm, a pellet shape and white color.
It could contain 0.00036 % < [Ti] < 0.0014 % and 0.0011 % < [Zn] < 0.0043 % by weight mainly due to the use of titanium dioxide (TiO_2) as an opacifier and whitener while zinc is likely present due to the use of zinc-based catalysts in the polymerization process.

b) Zinc oxide (ZnO)

The reaction was performed in the presence of zinc oxide (ZnO), which was used as a reaction catalyst. The ZnO had a particle size of 18 nm and a purity of 99.95 %.

c) Ethylene glycol (EG)

Ethylene glycol (EG) serves a dual function as it acts both as a medium where the depolymerization reaction takes place and as a reactant that interacts with vPET to produce the degradation products. It was acquired from VWR Chemicals with a purity ≥ 98%.

3. Results

The experimental procedure presented in Figure 2 is described as follows:

1. PET pellets were fed into the reactor along with ZnO catalyst and EG at room temperature, using the optimal reaction ratios of EG:PET molar ratio of 17:1 and a PET:ZnO molar ratio of 42:1. The reaction mixture was subjecoocted to microwave irradiation under controlled conditions (210°C, 10 bar) for 75 minutes with continuous stirring at 177 rpm. These conditions were identified as optimal based on preliminary experiments and literature review.

After the reaction period, stirring was stopped, and the reaction medium was cooled to 40°C within 15 minutes using its internal cooling system, followed by system depressurization.

2. The reaction medium was transported to the analytical laboratory, cooling to room temperature during transit.
3. Water was added to the reaction mixture, which was then heated to 80°C for 15 minutes to promote the dissolution of the formed BHET, while unreacted PET and ZnO remained in the solid state.
4. The mixture was filtered (approximately 15 minutes), naturally cooling to 60°C during the process.
5. The solid fraction (unreacted PET, ZnO, and residual moisture) was dried at 80°C for 7 hours under atmospheric pressure.
6. The liquid fraction was cooled to 5°C for 6 hours in a refrigerator to induce BHET precipitation.
7. Cold filtration was performed, and the precipitate was washed with cold water to remove EG residues from its surface.
8. The moist BHET was dried at 80°C for 7 hours under atmospheric pressure to obtain the final purified product.

A PET degradation efficiency of 97.2% was achieved, along with a BHET isolation yield of 86.6%, by means of the described process.

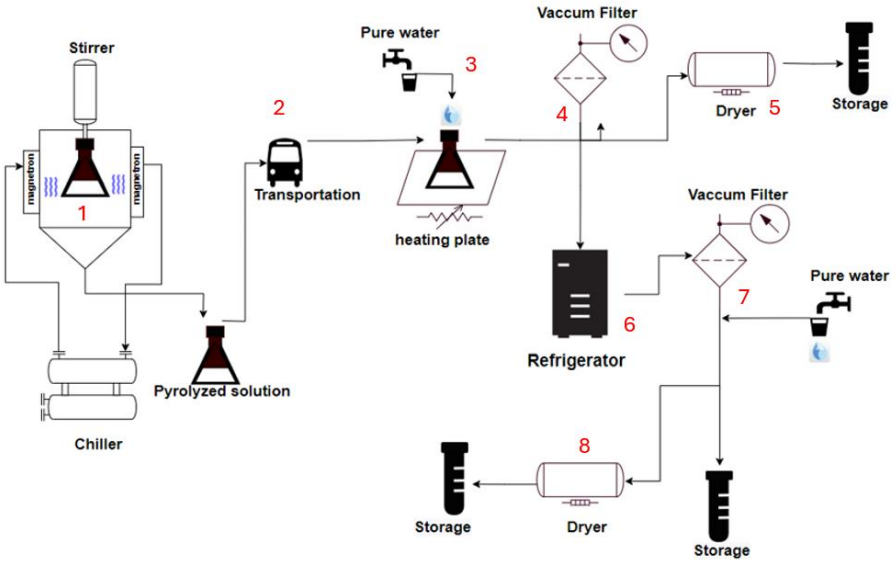

Figure 2. Laboratory procedures of microwave-assisted depolymerization of PET to obtain high-purity BHET.

4. Consideration for the scale-up process

The microwave heating presents various advantages over conventional heating, such as penetrating radiation, controllable electric field distribution, rapid heating, selective heat and self-limiting reactions.

Several key parameters were identified as critical for process optimization:

1. **Microwave Power**: The use of microwaves as a heating source resulted in a decrease in energy consumption to as low as 13.6 kWh/kg PET.
2. **Pressure**: Operating at 10 bar ensures that the EG remains in the liquid phase at the reaction temperature, which allows the reaction to proceed under optimal conditions.
3. **Stirring Rate**: A stirring rate of 177 rpm ensured uniform distribution of the reaction components and heat transfer.
4. **Cat:EG wt%**: A catalyst loading of 0.18 wt% proved to be sufficient for complete depolymerization while minimizing excess reagent use.

For industrial scale-up, several considerations were identified:

1. **Reactor Design**: Multi-mode cavity reactors with multiple magnetrons would be required to ensure uniform heating in larger volumes. This design is essential for maintaining product quality and process efficiency. Investment in specialized reactor designs will be necessary, potentially increasing initial capital costs but ensuring long-term process reliability.
2. **Continuous Processing**: A continuous flow system could enhance efficiency and facilitate integration with existing recycling infrastructure. Process parameters will need to be adjusted for continuous operation, potentially affecting residence time and catalyst interaction.
3. **Heat Recovery**: Implementing heat recovery systems could further improve energy efficiency by utilizing the heat generated during the condensation stages. Integrating heat recovery systems will require additional engineering considerations but will result in significant energy savings.
4. **Solvent Recovery**: Developing efficient EG recovery and recycling systems would enhance the economic and environmental sustainability of the process. Effective recovery reduces raw material costs and minimizes waste generation. Solvent recovery systems will be essential for maintaining the economic viability of the process at an industrial scale.

5. Conclusions

This study demonstrates the significant potential of microwave-assisted depolymerization for the sustainable recycling of PET. The process achieves high conversion rates and BHET yields while reducing energy consumption and processing time compared to conventional methods. The use of ZnO as a catalyst offers environmental advantages while maintaining excellent catalytic performance in the microwave environment. The conversion efficiency of PET to BHET using microwave-assisted glycolysis was significantly higher than that of conventional methods, achieving a conversion rate of 97.2% and a BHET yield of 86.6%. These results highlight the potential of microwave-assisted processes to enhance the efficiency of chemical recycling. The energy consumption of the microwave-assisted process was 13.6 kWh/kg PET, approximately 45% lower than conventional heating methods, primarily due to shorter reaction times and the inherent efficiency of microwave heating. Moreover, the characterization of the resulting BHET, conducted using nuclear magnetic resonance (NMR) spectroscopy, confirmed its chemical structure and a purity of 92.3%.

5.1 Future research should focus on:

Integrating this technology into existing recycling infrastructure could significantly enhance recycling rates and quality of recovered materials, contributing to a reduction in virgin plastic production and associated environmental impacts.

- **Catalyst innovation**: Development of catalysts designed specifically for the microwave environment, including supported metal nanoparticles and ionic liquids.
- **Process intensification**: Integration of microwave technology with advanced techniques such as continuous flow processing.
- **Valorization of complex PET waste**: Expanding microwave-assisted depolymerization to complex PET waste streams including colored, multi-layered, and contaminated PET.
- **Techno-economic analysis**: Comprehensive evaluation of the economic viability and environmental benefits of microwave-assisted depolymerization at industrial scales.
- **Sustainable catalyst recovery**: Development of efficient methods for catalyst recovery and reuse to further enhance the sustainability profile of the process.

The journey toward sustainable PET recycling through microwave-assisted depolymerization exemplifies how innovative technologies can address pressing environmental challenges while creating economic opportunities in the circular economy landscape.

6. Acknowledgements

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7. References

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