

THERMOCATALYTIC DEHYDROGENATION OF PLASTIC WASTES ASSISTED BY ZnCl_2 -BASED MOLTEN SALTS

Claudia Prestigiacomo¹, Dennis Ruvio¹, Najwa Hamdi¹, Tony Picaro², Onofrio Scialdone¹,
Alessandro Galia^{*1}

1 Dipartimento di Ingegneria, Università degli Studi di Palermo; 2 United Renewable Technologies

**Corresponding author: alessandro.galia@unipa.it*

Highlights

- A new process based on the use of molten ZnCl_2 is herein presented with the purpose of reaching negative CO_2 emissions in the field of plastic wastes management. This groundbreaking goal can be achieved by partitioning the carbon content of the waste in a valuable solid carbon material, while producing a hydrogen-rich gas phase through a low temperature-catalytic carbonization.
- Preliminary results confirmed that ZnCl_2 is an effective promoter of the dehydrogenation, improving the molar fraction of molecular hydrogen in the gaseous phase.

1. Introduction

The twenty-first century is characterized by two important challenges: the decarbonization of the global economy and the sustainable valorization of anthropogenic waste. Among these, single-use plastics (SUPs) pose a significant threat due to their persistence and detrimental impact on ecosystems. Conventional disposal methods contribute to high CO_2 emissions. Advanced waste valorization technologies like pyrolysis and gasification seem promising but they need downstream carbon capture processes for carbon neutrality [1]. Similarly, industrial hydrogen production from fossil fuels emits significant amounts of CO_2 . Thermochemical carbonization assisted by zinc-based molten salts mixtures, could emerge as an alternative valorization route [2]. This approach not only allows to convert waste carbonaceous matrices into valuable solids like biochar but also yields molecular hydrogen in the gas phase. Studies on sawdust carbonization reveal the ZnCl_2 's multifaceted influence, from depolymerization to aromatization [3]. Aim of our work is the investigation of the thermocatalytic carbonization of High Density Polyethylene (HDPE), as a model compound for SUPs, in the presence of molten ZnCl_2 as catalyst to produce molecular hydrogen and carbonaceous solid residues.

2. Methods

The catalyst employed in this process was ZnCl_2 ($\geq 97\%$, Technical Grade), purchased by VWR chemicals. The model compound for SUPs was HDPE Rigidex HD5502S, supplied by Ineos Group. Thermogravimetric analysis (TGA) were performed in Argon atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. Three reaction systems were employed to perform the tests:

- a static AISI 316 batch reactor (25 mL of internal volume);
- a static Pyrex glass batch reactor (200 mL of internal volume) to investigate the phase behavior of the reaction mixture;
- a stirred glass lined AISI 316L batch reactor (200 mL of internal volume) to investigate the effect of the fluid dynamic conditions on the figures of merit of the process.

The gaseous products collected at the end of each test were analyzed by a gas chromatograph equipped with a 15 ft Supelco 60/80 packed column and a TCD detector. A dehydrogenation index (DHI) was defined as the ratio of the moles of the H atoms globally detected in the gaseous products and that of the H atoms in the feedstock initially charged in the reactor. The solid products were recovered by filtration after the dissolution of ZnCl_2 in a 0.1 M HCl solution. Additionally, the carbon materials were washed

in water at 50°C for 24 h. A Perkin Elmer Series II CHNS Analyser was employed for elemental analysis of the solids.

3. Results and discussion

TGA of pure HDPE, pure ZnCl_2 and binary mixture HDPE- ZnCl_2 clearly showed the catalytic activity of ZnCl_2 since the mass loss rate of HDPE is improved when the salt is present. Preliminary experiments were carried out in the static batch reactor of 25 mL and they indicated that molecular hydrogen yield w/w % increased from 0.01% to 1.1% and the DHI increased from 0 to 1.84% when the reaction temperature increased from 300°C to 400°C with a reaction time of 30 min. Tests conducted in the Pyrex glass reactor to follow the phase behavior of the system during the heating allowed us to confirm that the reaction proceed through a reaction front in the static regime. Further experiments conducted in the stirred glass lined batch reactor of 200 mL, suggest that the phase behavior of the polymer-molten salt blend significantly affects the process performance. In fact when the carbonization was conducted at 400°C for 30 minutes, at an agitation speed of 200 rpm with a HDPE/ ZnCl_2 ratio of 2%, the DHI increased to 6%. Additionally, the gas phase exhibited a molar fraction of H_2 of approximately 60%. When the reaction time was increased to 60 min, the DHI further increased up to 16% with a H_2 molar fraction of around 45%. In these conditions, a solid carbon was produced with a H/C molar ratio of 0,39.

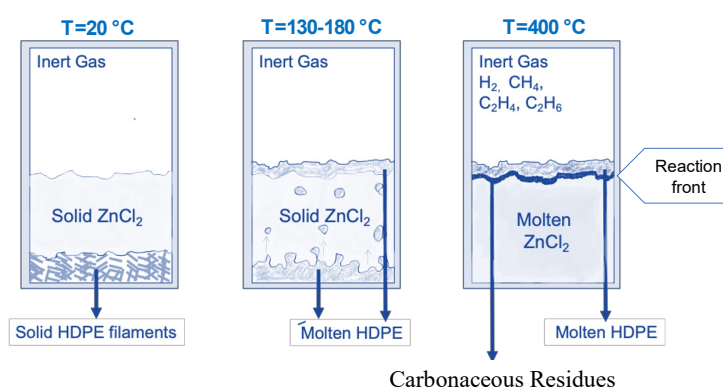


Figure 1. Phase behavior of the mixture observed in tests performed in a glass reactor.

4. Conclusions

The previous findings have shown that it is feasible to carbonize HDPE using zinc-based molten salts as both catalyst and reaction medium, even under relative mild conditions. However, additional research is required to assess the characteristics of the solid residue and to explore the operational limitations of the process.

References

- [1] E.M. Lozano, T.H. Pedersen, L.A. Rosendahl, Integration of hydrothermal liquefaction and carbon capture and storage for the production of advanced liquid biofuels with negative CO_2 emissions, *Applied Energy* 279 (2020) 115753.
- [2] S. Chen, L. Zheng, S. Jiang, H. Hou, Carbonisation: A feasible route for reutilization of plastic wastes, *Science of the Total Environment* 710 (2020) 136250.
- [3] F. Lin, X. Liu, M. Ma, F. Qi, Y. Pan, L. Wang, P. Ma, Y. Zhang, Real-time monitoring the carbonization and activation process of activated carbon prepared from Chinese parasol via zinc chloride activation, *J. Anal. Appl. Pyrolysis* 155 (2021) 105089.

Keywords

Catalytic carbonization, hydrogen production, molten salts, circular carbon economy.