Thermodynamic study of pyrolysis and in line dry reforming of waste plastics for syngas production

Leire Olazar[1*], Laura Santamaria[1], Santiago Orozco[1], Maria Cortazar[1], Enara Fernandez[1], Maite Artetxe[1], Gartzen Lopez[2]

1 Department of Chemical Engineering, University of the Basque Country, UPV/EHU, P.O. Box 644-E48080 Bilbao, Spain; 2 IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

**Corresponding author: leire.olazar@ehu.eus*

Highlights

- Equilibrium simulation was approached to analyze process performance.
- Results clearly show that a strict control of process conditions is required.
- Polyolefins are those of highest potential for syngas production.

1. Introduction

Plastic pollution is causing great ecological impact in terrestrial and aquatic environment. Its presence is regarded as enduring, with removal rates ranging from decades to centuries. Thermal treatments have become standard processes in industry for chemical recycling. Pyrolysis, pyrolysis-gasification, pyrolysis-steam reforming and pyrolysis-dry (CO_2) reforming are the main processes for recycling plastics with the aim being the production of H_2 and synthesis gas [1]. There are hardly studies focused on technologies like pyrolysis and in line dry reforming [2, 3], and there are no records of continuous processes in the available literature. The pyrolysis and in line dry reforming can generate syngas, which can then be converted into fuels and high-value chemicals. The aim of this study is to explore the potential of pyrolysis and in line dry reforming of waste plastics.

2. Methods

The simulation of dry reforming was conducted using as feed the products obtained in the fast pyrolysis in earlier experimental studies conducted in a CSBR stage together with the reforming agent stream. The reforming of fast pyrolysis volatiles was assessed using the Gibbs free energy minimization approach to analyze the product distribution. This approach is based on solving the mass and energy balances that minimize Gibbs free energy, i.e., those that correspond to the equilibrium situation. This tool has the capability to accurately predict experimental results for various process conditions, particularly when full conversion of pyrolysis volatiles is achieved [4, 5]. The Pro II 10.1 simulation program, along with the Soave-Redlich-Kwong equation of state, were used in the study. The reactor was assumed to be isothermal, and the reaction conducted under constant pressure conditions.

3. Results and discussion

The effect of temperature was analyzed for a feed of HDPE in the range from 600 ºC to 800 ºC and that of CO_2/C ratio in the rage of 1 to 3. An increase of both temperature and CO_2/C ratio improve CH_4 conversion. However, the presence of unreacted CO_2 promotes the reverse WGS reaction at high temperatures, leading to the formation of water. In this respect, the highest H_2 concentration and production is obtained operating at a temperature of 800 ºC and using a CO_2/C ratio of 1.

Fig. 1 (a) shows the syngas composition predicted in the pyrolysis and in line dry reforming of different plastics at 700 ºC with a CO_2/C ratio of 1.5. Given the similar composition of HDPE and PP pyrolysis streams, a similar gas composition is obtained. However, PS derived products are mainly of aromatic nature, and therefore these hydrocarbons have higher C/H ratios. Accordingly, the syngas obtained in their reforming has lower H_2 contents, but higher of CO. Finally, PET leads to a syngas with the lowest H_2 concentration. It is to note that this polymer has a rather high O content, and remarkable yields of CO_2 are therefore obtained in the pyrolysis step.

Fig. 1 (b) shows the H_2/CO ratios obtained in the synthesis gas in the dry reforming of HDPE at various temperatures and CO_2/C ratios. As observed, there is a significant increase in this ratio as temperature is raised for a given CO_2/C ratio. It is to note that the H_2 content of the plastics limits the ceiling H_2/CO ratio that may be obtained in the dry reforming. Nevertheless, the combined dry/steam reforming is a promising alternative to overcome this limitation.

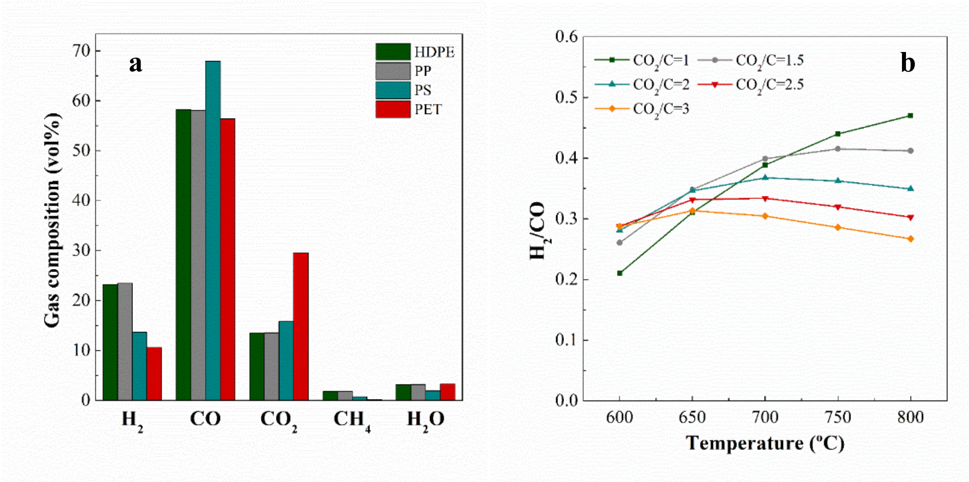

Figure 1. (a) Composition of the gaseous stream obtained in the dry reforming of different plastics pyrolysis volatiles at 700 ºC with a CO_2/C ratio of 1.5. (b) Evolution of H_2/CO ratio with temperature in the syngas for different CO_2/C ratios.

By incorporating steam into the dry reforming of plastic wastes, H_2/CO molar ratio may be tuned, thereby enabling customization of the syngas quality to meet specific requirements for various industrial applications. In the case of polyolefins, the production of a syngas with a ratio of $H_2/CO = 1$ is straightforward, as a feed with a S/C ratio of 0.6 is sufficient. In the case of polystyrene, the S/C ratio must be increased considerably (0.8) to achieve the desired ratio. However, in the case of PET, this ratio was not achievable, as this polymer has a high O content and a low of H, making it difficult to achieve a high H_2/CO ratio.

4. Conclusions

This process is of great environmental interest in terms of CO_2 valorization and waste management. The dry reforming of HDPE pyrolysis volatiles is highly sensitive to process conditions. In fact, variables such as temperature and CO_2/C should be adjusted simultaneously to ensure process efficiency. The polymers with high H_2 content, such as polyolefins, have a great potential for H_2 production in the pyrolysis and dry reforming process. Thus, H_2 productions higher than 11% may be obtained under suitable conditions, with the H_2/CO ratio of the syngas being of around 0.5. The combined dry-steam reforming was studied in order to increase the H_2/CO ratio of the syngas and improve its potential for certain applications. Overall, the pyrolysis and in line reforming process has a huge potential for the joint valorization of CO_2 and waste plastics and produce a syngas that may be used as a feedstock for further chemical processes.

References

[1] L. Santamaria, G. Lopez, E. Fernandez, M. Cortazar, A. Arregi, M. Olazar, Energy Fuels 35 (2021) 17051-17084.

[2] M. Al-asadi, N. Miskolczi, J. Energy Inst. 96 (2021) 251-259.

[3] J.M. Saad, P.T. Williams, Fuel Process. Technol. 156 (2017) 331-338.

[4] M. Cortazar, N. Gao, C. Quan, M.A. Suarez, G. Lopez, S. Orozco, L. Santamaria, M. Amutio, M. Olazar, Fuel Process. Technol. 225 (2022) 107044.

[5] G. Lopez, I. Garcia, A. Arregi, L. Santamaria, M. Amutio, M. Artetxe, J. Bilbao, M. Olazar, Energy Convers. Manage. 214 (2020) 112889.

Keywords

Hydrogen, CO_2, Pyrolysis, Waste plastics.