

Abstract

Nowadays, the pyrolysis process has emerged as an economically viable alternative to incineration, offering a substantially reduced environmental footprint. This conversion method not only provides an eco-friendly solution for managing plastic waste but also produces a liquid product suitable for various energy-related applications. With the growing demand for diesel fuel in European countries and the United States, the pyrolysis of waste plastics has attracted worldwide attention in recent years. However, the crude liquid product obtained through pyrolysis requires an additional upgrading step, such as hydrogenation, to meet the requirements for diesel fuel. In this PhD thesis, the potential of catalytic methane decomposition as an environmentally friendly technology for producing hydrogen to upgrade plastic pyrolysis oil (PPO) has been investigated.

The initial segment of this research project was dedicated to exploring the potential of the pyrolysis process for producing diesel fuel from Mixed Waste Plastic (MWP). MWP, sourced from various origins, comprises a variety of polymers including Polyethylene Terephthalate (PET), High-Density Polyethylene (HDPE), Polyvinyl Chloride (PVC), Low-Density Polyethylene (LDPE), Polypropylene (PP), and Polystyrene (PS). Under appropriate operating conditions of 450-500 °C and a heating rate of 10 °C/min, MWP could yield over 50 wt.% of liquid product, if the PET and PVC content in the mixture remain below 10 wt.% and 5 wt.%, respectively. The utilization of suitable catalysts such as Fe-PILC can further elevate the liquid yield to nearly 80 wt.%. Additionally, apart from affecting the liquid product yield, the choice of catalyst also influences the quality of the liquid oil. Silica-alumina, FCC, and zeolite catalysts are conducive to producing a liquid oil with a low hydrocarbon chain length (C5-C12) and a high aromatic content or olefinic compound. Conversely, the application of Fe-, Ti-, Zr-, and Al-pillared clays enhances the yield of diesel-range hydrocarbons while increasing the paraffinic content in the liquid product. A comparison of the characteristics of 19 different PPOs documented in the literature with the standard physicochemical properties of marine diesel fuel revealed that the liquid oil obtained from the pyrolysis of waste plastic could potentially be used as fuel for marine diesel engines with just a modification of the flash point through distillation processes. However, PPO typically contains unsaturated compounds, rendering the produced fuel unsuitable for combustion in light-duty diesel engines.

The hydrogenation process proves instrumental in enhancing the quality of this oil by converting unsaturated compounds, such as olefins present in PPO, into paraffins. The hydrogen required for upgrading PPO can be sourced from methane, and methane cracking over carbon-based catalysts derived from waste materials presents an environmentally friendly solution for providing hydrogen in this system. Consequently, the primary focus of the second section of this thesis was dedicated to evaluating the catalytic potential of chars produced from digestate, sewage

sludge, and wood for methane pyrolysis, aiming to provide a hydrogen feed stream for the hydrogenation of PPO. The results from methane cracking over these chars revealed that carbon materials with lower levels of ash content exhibited higher methane conversion, with the sequence being Wood char > Digestate char > Sewage sludge chars. Due to this issue, ash removal through the leaching process by HNO_3 was performed on three chars with different levels of ash content (digestate char and two sewage sludge chars). After the leaching process, methane conversion under operating conditions of 900°C , a volume hourly space velocity (VHSV) of 3 L/g.h, and a $\text{CH}_4:\text{N}_2$ ratio of 1:9 increased by 10 mol.%. Additionally, methane conversion improved by 15-20 mol.% through the physical activation of wood char and three leached chars produced from digestate and sewage sludge. An initial methane conversion rate of around 80 mol.% was observed during methane cracking over all four upgraded chars under similar operating conditions. An evaluation of hydrogen production via the pyrolysis of pure methane at a temperature of 900°C and a VHSV of 3 L/g.h indicates that a gas stream with a hydrogen purity of 45 mol.% could be attained through methane cracking over upgraded chars derived from biomass (wood) and waste (sewage sludge).

The last section of this project was devoted to the design and simulation of a Pressure Vacuum Swing Adsorption (PVSA) system aimed at enhancing the purity of hydrogen and the recovery of unreacted methane. The results of the design and simulation of this gas separation unit indicate that the optimal operating conditions for the PVSA system are a dimensionless space velocity (SV) of 4, a feed pressure of 6 atm, and a regeneration pressure of 0.15 bar. Under these operating conditions, two gas product streams are generated: one stream with a hydrogen purity of 91 mol% and a hydrogen recovery of 86 mol%, utilized for the hydrogenation of PPO; and another stream with a methane concentration of 82 mol% and a methane recovery of 96 mol%, recycled back into the methane cracking unit. The gas separation unit requires a total power consumption of 142 W/mol_{feed} to operate effectively under these conditions. Recycling unreacted methane back into the methane cracking unit increases hydrogen purity to 94.5 mol% and reduces total power consumption to 137 W/mol_{feed}. Based on this process, for the continuous production of upgraded PPO at a flow rate of 1 kg/h, the system requires 1.56 kg/h of plastic waste, 268.434 NL/h of methane, and 28.46 kg/h of sewage sludge. Additionally, in this system, the CMD unit can produce 8.615 kg/h of carbon-enriched biochar which can be utilized in the carburization of iron ore in the steel-making industry.