

MIXED PLASTIC PYROLYSIS CATALYSED BY ZINC OXIDE

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KEY FINDINGS

Pyrolysis is one of the possible solutions to the increasing amount of mixed plastic waste (unrecyclable) in landfills. This project focused on the utilization of a ZnO catalyst and decreased pressure in the optimization of the plastic pyrolysis conditions. A relatively low temperature of 450°C and pressure of 0.42-1.5 bar were used to study the pyrolysis of LDPE, HDPE and PP and mixtures of the abovementioned plastic types. The presence of the catalyst and low pressure influenced the yields of different pyrolysis product types and also decreased the process time significantly. A novel pilot plant based on the fluidized bed reactor was designed, built and commissioned during this project, allowing to further study of the potential of ZnO catalyst in the plastic pyrolysis.

INTRODUCTION

Plastic waste has become a significant contributor to municipal solid waste streams. Due to the nonbiodegradable nature of plastics, the amount of this type of waste increases annually. The most common types of plastic are low- and high-density polyethylene (LDPE, HDPE) and polypropylene (PP), which were taken under consideration during this study. Those types of plastic are commonly used in the form of bottles, mixed with foil and other types of packaging used by millions of humans on a daily basis.

To address the plastic pollution issue, novel solutions must be implemented. One of the solutions proposed in this project is the pyrolysis of mixed plastic waste. Pyrolysis is the process of thermal decomposition of materials in the absence of oxygen. This prevents the incineration of the material and the generation of carbon dioxide among other harmful products of plastic combustion. In the case of plastic pyrolysis, the decomposition process of the long hydrocarbon chains leads to many useful products in the form of oils, waxes and char.

To decrease the time and the temperature of the thermal decomposition, the influence of decreased pressure and a zinc oxide (ZnO) catalyst were studied. Additionally, a novel fluidised bed pyrolysis reactor was designed and commissioned to perform pilot plant-scale pyrolysis experiments. A to-scale process processing 100 kg/hr of mixed plastic waste was then

designed using Aspen Plus® simulation software, and a technology review at scale was conducted.

METHODOLOGY

Two separate sets of experiments were conducted: Laboratory scale and pilot plant scale. In laboratory-scale experiments, 15 g of plastic pellets were placed in the round bottom flask equipped with a heating mantle, thermometer, condenser and receivers. The first set of experiments focused on individual and mixed plastics (HDPE, compounded LDPE and PP). Each type of plastic was treated three times, without the addition of the catalyst, with 5:100 ZnO and with 10:100 ZnO mass-wise. All experiments were conducted under pressure of 0.42 bar at a temperature of 450°C. Products were then analyzed using a gas chromatograph equipped with a mass spectrometer (GC-MS). For each run, the reaction time and product yields were recorded.

The pilot plant was designed, built and commissioned during this project. The fluidized bed reactor was chosen. The reactor was then equipped with a hopper and a screw feeder, allowing for constant addition of fresh feed material into the reaction zone. Gaseous products leaving the reactor were then separated from solid particles using a cyclone and condensed to liquid and wax fractions using a series of heat exchangers. Each run utilized 220 g of ZnO catalyst and various masses of different plastic pellets (150 g of LDPE and 400 g of HDPE and PP each). The catalyst

was placed in the reactor before the run began, while plastic pellets were fed into the reactor using a feeding system. Products were collected from the receivers and analyzed using GC-MS. For each run, product yields were recorded.

In the simulated design, a scaled fluidized-bed reactor system with cyclone and relevant cooling was designed using rigorous unit operations in Aspen Plus®. The energy requirements for the process were established, along with the costs of the unit operations.

MAIN RESULTS

The laboratory scale experiments utilizing individual plastic samples showed that at the given conditions, the catalyst-to-feed ratio has an influence on the yields of types of products obtained during the pyrolysis. For compounded LDPE, the increasing catalyst-to-feed ratio allowed for an increase in the total oil and wax product yields from 69.5 wt% for uncatalysed pyrolysis to 78.3 wt% for 5:100 catalyst-to-feed ratio. The gaseous emissions were decreased from approximately 20 wt% to 10 wt% for both catalyzed experiments. Contrary to LDPE, in HDPE pyrolysis experiments, the increased amount of catalyst resulted in a decrease of the combined oil and wax products from 85.4 wt% to 72.3 wt%. A larger quantity of gaseous emissions was observed with the increase in catalyst-to-feed ratio (6.4 wt% to 17.6 wt%) as secondary cracking was likely catalyzed. Polypropylene experiments showed that the catalyst-to-feed ratio had no influence on the liquid product yields (approximately 72 wt%). However, gaseous emissions decreased from 19.2 wt% for the uncatalysed experiment to 17.7 wt% for the 10:100 catalyst-to-feed ratio experiment, with an increase in char yield from 9.3 wt% to 10.2 wt%.

Three plastic mixtures containing different wt% of LDPE, HDP and PP were prepared (see Figure 1).

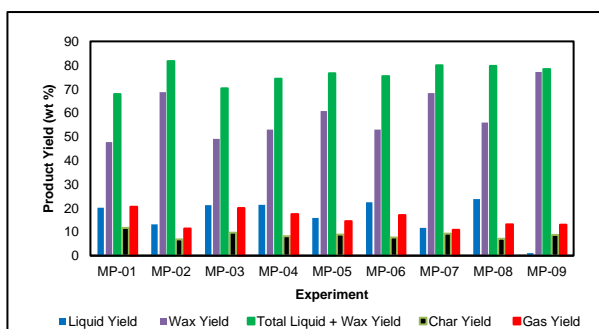


Figure 1. Comparison of product yields for uncatalyzed and catalyzed plastic pyrolysis experiments using mixed feedstock of LDPE, HDPE, and PP pellets.

The first one contained 15 wt% LDPE, 45 wt% HDPE, 40 wt% PP. For the abovementioned composition, the highest yield of oil and wax combined was achieved for a 5:100 catalyst-to-feed ratio (81.7 wt%). A higher amount of catalyst generated results similar to the uncatalysed experiment. A similar trend was observed for the second mixed plastic sample containing 32.3 wt% LDPE, 34.52 wt% HDPE, and 33.18 wt% PP. The third mixed plastic sample was composed of 65 wt% LDPE, 20 wt% HDPE, and 15 wt% PP. The combined liquid and wax yields decreased from 80.0 wt% to 78.3 wt% with the increase in the catalyst-to-feed ratio. However, the presence of ZnO increased gaseous emissions yields from 10.1 wt% to approximately 13.0 wt% for both catalysed experiments. The presence of a ZnO catalyst influenced reaction times significantly. The addition of a catalyst allowed for the decrease of the overall process time to 14 hours for the 5:100 catalyst-to-feed ratio experiment and further to 11 hours for the 10:100 catalyst-to-feed ratio experiment. Reaction times recorded for HDPE and PP were significantly shorter than those recorded for compounded LDPE.

The experiments conducted using a pilot-scale pyrolysis plant revealed that for the LDPE experiment, most of the products received were in the form of gas. Approximately 51 wt% of the plastic sample was converted into volatiles, which was not captured by heat exchangers. The yield of oil and wax combined was 31.6 wt%, and the yield of the remaining char was 17.5 wt%. According to the collected data, only 80 wt% of the total LDPE mass reacted during a 1-hour long experiment. The HDPE experiment conducted a feed of 400g of plastic. The full conversion was achieved, yielding approximately 25.6 wt% of oil and wax, 15.9% of char and 58.9 wt% of gas. The polypropylene pyrolysis experiment yielded the highest amount of liquid and wax products combined (33.2 wt%) and the lowest gaseous emissions (20.8 wt%). The remaining mass of PP was transformed into char.

The to-scale process (see Figure 2) was modelled using the rigorous fluidized bed reactor model on Aspen a combination of available kinetic data from literature, and the data determined in the phase 1 kinetic study in this work using lumped parameters for component classes of wax, liquid oil, char and gas. Each plastic type was modelled uniquely as a non-conventional component, based on the monomer constituent and density. The detailed reactor model design used, allows for more precise estimates of the minimum fluidization velocity, the reactor length and diameter,

flow rates, pressure drops and sensitivities. The quantity and composition of the reaction products were also calculated rigorously. This information is very useful for the to-scale process design.

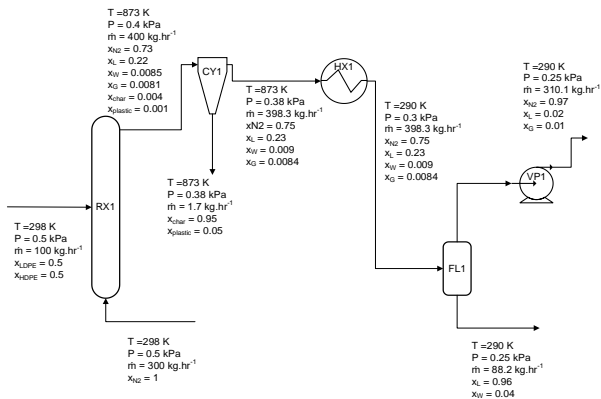


Figure 2. Model of the proposed pyrolysis process with reactor run at 723-873 K. T- temperature, P- pressure, \dot{m} - mass flow rate, x_i - mass fraction. RX1- Fluidized bed reaction, CY1- cyclone, HX1- Heat exchanger, FL1- Flash vessel, VP1- vacuum pump.

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