# A Fuel Oil Production Plant Through Pyrolysis of the Waste High-Density Polyethylene

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*Abstract:* -This study examined the production of synthetic fuels (pyrolytic oil) through the pyrolysis of the waste high-density polyethylene (HDPE). An ideal mixed reactor was designed for the pyrolysis of the waste HDPE in the absence of a catalyst at a residence time of 60 minutes and a final temperature of 450 °C. At the end of the process, 81.32 kg/h liquid product, 18.48 kg/h gaseous product and 0.2% carbonic residue were obtained, respectively. The oil obtained by pyrolysis is a highly flammable dark brown liquor with a density of 772.6 kg/m3 and a pH of 5.5. ASPEN Hysys V11 and UNISIM were used to simulate the pyrolysis process. From the results, we have that ASPEN HYSYS is the proper simulator for the procedure, giving more accurate values. The simulation results revealed an oil yield of 82.9%, a gas yield of about 16.8%, and a carbon yield of <1%. The simulation revealed the onset of the reaction at about 325 °C with an optimum reaction temperature of 450 °C. If HDPE is correctly simulated, it is an excellent pyrolysis feedstock.

*Keywords**:** HDPE, recycling, pyrolysis, simulation, ASPEN HYSYS, UNISIM.*

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# 1-Introduction

Plastic adaptability and various other characteristics, such as lightweight, durable, flexible and cheap manufacturing, have led to widespread use [1-4]. Plastics are usually made through industrial systems. Most modern plastics are derived from chemicals related to fossil fuels, such as natural gas or oil; however, recent industrial methods use variants made from renewable materials, such as corn or cotton derivatives [5-8]. In 2020, 400 million tons of plastic were produced. If global plastic demand trends continue, it is estimated that by 2050, annual global plastic production will reach over 1,100 million tonnes. The success and dominance of plastics since the beginning of the 20th century have caused widespread environmental problems due to their slow decomposition rate in natural ecosystems [9-11]. Towards the end of the 20th century, the plastics industry promoted recycling to alleviate environmental concerns. Plastic pollution can be found, for example, creating patches of debris throughout the world's oceans and contaminating terrestrial ecosystems. Of all the plastic thrown away so far, about 14% is incinerated, and less than 10% is recycled [12]. In developed economies, about a third of plastic is used in packaging and about the same in buildings in applications such as piping, plumbing or siding. Other uses include automobiles (up to

20% plastic), furniture and toys [13-15]. In medicine, polymer implants and other medical devices are derived from plastics, at least in part. Today's most common plastic is polyethene or polyethene (abbreviated PE; IUPAC name polyethene or poly(methylene)). It is a polymer mainly used for packaging (plastic bags, plastic films, geomembrane containers including bottles, etc.) [16-18]. As of 2017, over 100 million tons of polyethylene are produced annually, accounting for 34% of the total plastics market. Many types of polyethylene are known, most of which has the chemical formula $(C2H4)n$. PE is usually a mixture of similar ethylene polymers with different 'n' values. High-density polyethylene (HDPE) is a thermoplastic polyethylene made from petroleum. To produce 1 kg of HDPE, 1.75 kg of oil is needed (in terms of energy and raw materials). HDPE is usually recycled and has no. "2" as its recycling symbol. HDPE is the third largest plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. Demand for HDPE has grown 4.4% in a year.

## 2. Materials and Methods

### 2.1. Recycling of plastic waste

Plastic materials make up an ever-increasing percentage of municipal and industrial waste going to landfills. Due to the large amount of plastic waste and environmental pressures, plastic recycling has become a dominant topic in today's plastics industry. Developing technologies to reduce plastic waste that is environmentally acceptable and cost-effective has proven to be a difficult challenge due to the inherent complexities in polymer reuse. Creating optimal processes for the reuse/recycling of plastic materials thus remains a worldwide challenge in the new century. Plastic materials find application in agriculture and plastic packaging, which is a high-volume market due to the many advantages of plastic over other traditional materials. However, such materials are also the most visible in the waste stream and have received much public criticism as solid materials have relatively short life cycles and are usually non-degradable.

There are four main approaches to recycling plastic waste: primary, secondary, tertiary and quaternary (ASTMD, 2000).


Fig. 1. Different methods of recycling plastic waste.

### 2.2. Thermal pyrolysis

The chemical recycling method, also called pyrolysis, is one of the most efficient and effective methods of recycling plastic; simultaneously, it converts plastic waste into fuel. Most recycling processes are expensive, energy-intensive and produce low-quality products. Pyrolysis is a sustainable waste management process and an environmentally friendly approach to treat solid plastic waste containing carbonaceous materials such as plastics and biomass. Pyrolysis, also called thermolysis, derived from the Greek (pur = fire; thermos = warm; luo = loosen), is a process which thermally decomposes higher molecular carbon compounds to produce lower molecular compounds in an oxygen-free environment at a temperature significantly high. Pyrolysis products are condensable gases, carbon residues and non-condensable gases. Steam consists of condensable gases that turn into liquefied gases (pyrolytic fuel) after condensation, while non-condensable are collected or vented as gases. Pyrolysis can occur at different temperature levels, reaction times, and pressures and in the presence or absence of catalysts. Plastic pyrolysis consists of low temperature (<400°C), medium temperature (400-600°C) or high temperature (>600°C). However, the optimum temperature range (450°C) was predicted in our paper. Steady-state simulation's purpose is to mimic any chemical process's performance. Process characteristics (e.g., flow rates, compositions, temperatures, pressures, properties, equipment sizes, etc.) are predicted using analytical techniques.

These techniques include mathematical models, empirical correlations, and computer-aided process simulation tools (such as Aspen Hysys), which is computer-aided software that uses fundamental physical relationships (e.g., material and energy balances, thermodynamic equilibrium, etc.) to predict process performance (e.g. flow properties and operating conditions). Therefore, in process simulation, we are given the process inputs and flow diagram and asked to predict the process outputs. Simulation of the pyrolysis process is attracting attention due to the growing interest in the pyrolysis of plastic waste for the production of fuels. In this present study, the simulation of plastic waste, such as HDPE, was carried out in the Aspen HYSYS V11 and UNISIM simulator. The Aspen HYSYS V11 simulator was chosen for this work because this simulator can perform and handle feedstock conversion. The study will give an idea of the compositions of the various products expected from the pyrolysis of plastic waste, which will help an interested researcher to know the expected outcomes and their compositions.

Pyrolysis oil is the final product of pyrolysis of waste plastics; the oil is widely used as an industrial fuel to replace furnace oil or industrial diesel. It is a tar type and is usually challenging to consider as a pure hydrocarbon. In typical industrial applications of pyrolysis oil as a fuel, the fuel oil is mainly used in machinery that does not require high-quality fuel oil. Converting plastic waste into energy will cause no pollution and solid waste.

The final product of the pyrolysis plant is oil, black carbon and release gas. Pyrolysis oil is mainly fuel oil used in heavy industries such as construction, steel, cement, and boiler factories. Pyrolysis oil is primarily used as a fuel for heating in heavy sectors; it is usually used in industries or machinery that do not require high-stability oil, such as steel, cement, brick, and glass factories, especially in steel and cement plants.

## 3. Practical pyrolysis work

The reaction sequence for this simulation is simple: the raw material HDPE is directly and simultaneously converted into products such as gas, pyrolytic oil, and charcoal. This model does not possess any secondary reactions as it is considered that the fast pyrolysis of the plastic does not occur in sufficient time to include secondary reactions between the products. The response is assumed to occur only in the vapour phase.

$$\text{HDPE} \longrightarrow H_2 + CH_4 + C_2H_4 + C_2H_6 + C_3H_8 + C_4H_{10} + C_5H_{12} + \text{pyrolytic oil} + 5C$$

The kinetics of plastic pyrolysis reactions have previously been successfully implemented with the Arrhenius equation. The kinetic parameters obtained were used for this simulation. The reported values are A = $1.71.10^{11}$s-1 and 77.2 KJ/mol.

Where K (s-1) is the rate constant, A (s-1) is the pre-exponential factor, E (KJ/mol) is the activation energy, T (K) is the temperature, and R is the universal gas constant 8,314 KJ/molK.

The procedures used to simulate the pyrolysis process with the help of Simulation computer software ASPEN HYSYS V11 and UNISIM are described below.

*Selection of components***.** Components, both reactants and products, were selected from the pure components section of the component list and added to the details in the component list based on the reaction described below. The simulator database does not contain polymers, so HDPE must be entered as a hypothetical component. Its density is 940 kg/m^3, and its boiling point is 270C.

*Selection of fluid package***.** After selecting the component list, the fluid package used to evaluate the physical properties of the components was also selected from the properties environment. The Fluid package used in this work was chosen as the Peng-Robinson model.

*The development of the pyrolysis reaction***.** After selecting the fluid package for the process, the reaction involved in the process was developed according to:

$$HDPE \longrightarrow H_2+CH_4+C_2H_4+C_2H_6+C_3H_8+C_4H_{10}+C_5H_{12}+\text{pyrolytic oil} +5C$$

The response was attached to the fluid box chosen, Peng-Robinson, before running in the simulation environment. *Simulation environment***.** After each step is preceded, we then enter the ASPEN HYSYS and UNISIM simulation environment. The process flow diagram was developed by selecting pieces of equipment from the pallet in ASPEN HYSYS/UNISIM and connecting them appropriately. The pyrolytic and the conversion reactor were also selected from the column section of the pallet, and the condenser was chosen from the standard selection of the pallet. After developing the flow diagram described above was simulated using the mass flow rate of 100 kg/hr of HDPE plastic waste at the optimum temperature of 450C and a pressure of 1 atm as feed to the pyrolytic reactor. The vapor-liquid fraction leaves the upper stream of the pyrolytic reactor, which contains oil and gas products, while carbon residues are separated in the bottom stream, leaving the reactor. The obtained vapour-liquid part is then introduced into the condenser to separate the gaseous fraction and the liquid fraction from obtaining the high purity of the desired product, which turns out to be liquid fuel.

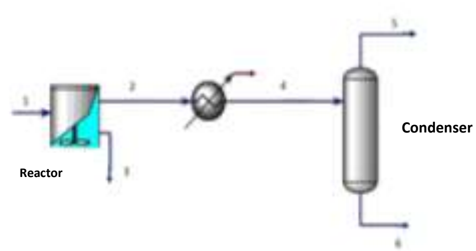



Fig. 2. Scheme of the simulation.

The scheme above represents the technological process of thermal pyrolysis. This process consists of a pyrolytic reactor and a condenser. Stream 1 is the feed stream and contains the polymeric material. The decomposition of this material takes place in the reactor into C1-C4 hydrocarbons, hydrogen, pyrolytic oil and carbonaceous components. The carbonaceous parts leave the bottom stream of the reactor (stream 3), while the other members leave as vapours from the upper stream (stream 2). This stream is then sent to the separator, where pyrolysis gases (stream 5) and pyrolytic oil (stream 6) are separated by condensation.

## 4. Results and Discussions

**4.1. Process simulation** using ASPEN HYSYS has given the following results as in Table 1.

Table 1. Material streams.

| | *Unit* | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| Vapour Fraction | | 1 | 1 | 0 | 0.47 | 1 | 0 |
| Temperature | *C* | 320 | 451. | 451 | 200 | 200 | 200 |
| Pressure | *kPa* | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 |
| Molar Flow | *kmol /h* | 0.01 | 0.28 | 0.01 | 0.28 | 0.13 | 0.1 |
| Mass Flow | *kg/h* | 100 | 99.8 | 0.15 | 99.8 | 16.8 | 82. |
| Liquid Volume Flow | *$m^3$/h* | 0.10 | 0.13 | 9E-05 | 0.13 | 0.02 | 0.1 |
| Heat Flow | *kJ/h* | -73307.9 | -73386.8 | 79.2 | -154638 | -25469 | -129169 |

The table above shows the simulation results of the thermal pyrolysis of HDPE. As we noticed, the results are close to the preliminary theoretical calculations of each current. As predicted, 450$^{o}$ C is the optimal temperature for achieving the maximum process yield. The pressure is maintained at 1 atm. From pyrolysis, we get less than 1 kg/h of carbonic waste as the bottom stream and 99.8 kg/h of the top stream as steam, sent to the condenser where pyrolytic oil and gases are separated. We get 83 kg/h of pyrolytic oil from the condenser from 86 kg/h, which was predicted in the theoretical calculations. So, high accuracy is achieved in this simulation model.

Table 2 Following the process simulation, we got the chemical composition of the streams:

| Streams | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **Composition** Mole Fraction | | | | | | |
| H2 | 0 | 0.044 | 0 | 0.044 | 0.094 | 0.00 |
| Methane | 0 | 0.044 | 0 | 0.044 | 0.094 | 0.00 |
| (Ethane) | 0 | 0.044 | 0 | 0.04 | 0.09 | 0.00 |
| Propane | 0 | 0.044 | 0 | 0.044 | 0.093 | 0.00 |
| i-Butane | 0 | 0.044 | 0 | 0.044 | 0.092 | 0.00 |
| n-Butane | 0 | 0.044 | 0 | 0.044 | 0.092 | 0.01 |
| i-Pentane | 0 | 0.044 | 0 | 0.044 | 0.090 | 0.01 |
| n-Pentane | 0 | 0.044 | 0 | 0.044 | 0.090 | 0.00 |
| (Carbon) | 0 | 0 | 1 | 0 | 0 | 0 |
| (HDPE*) | 1 | 1.65E-10 | 0 | 1.65E-10 | 6.39E-11 | 2.54E-10 |
| (Oil*) | 0 | 0.599 | 0 | 0.599 | 0.163 | 0.98 |
| Ethylene | 0 | 0.044 | 0 | 0.044 | 0.094 | 0.00 |

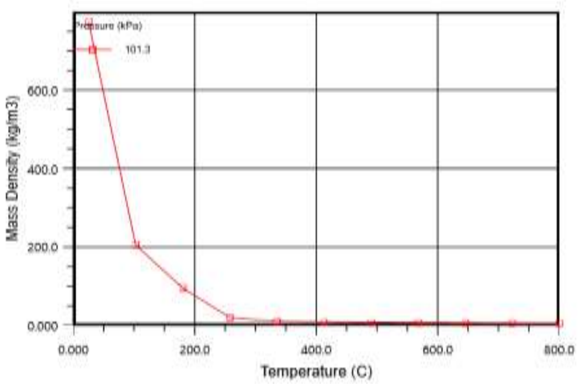
The table presents the composition of each stream and the fractions of the components in each stream. Stream 1 is the feed stream, so it contains only polymeric material. The entire carbonaceous composition leaves the reactor through stream 3, while stream 2 includes the other hydrogen components, C1-C4, pyrolytic oil in the gaseous phase and traces of HDPE. In the condenser, this stream is divided into a gaseous stream (stream 5) where the most significant amount is occupied by gases, $H_2$, C1-C4, a small amount of pyrolytic oil and traces of HDPE. The bottom stream consists of 98% pyrolytic oil; the rest is a small unit of oil and traces of PE. $m_{oil} = 82.98x0.98 = 81.32\ kg/h$

$$p = \frac{81.32}{82.98} x\, 100 = 97.9\%$$

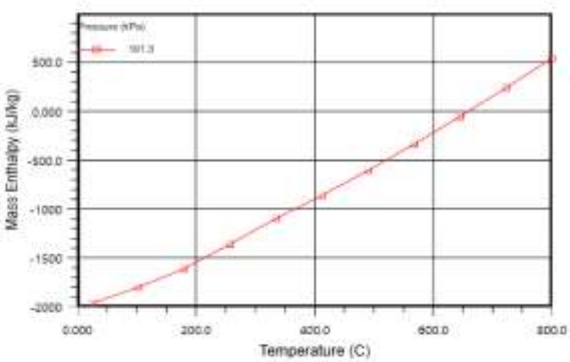
So, in the end, it resulted in an amount of 81.32 kg/h pyrolytic oil with 97.9% purity.

Table 3. Energy balance.

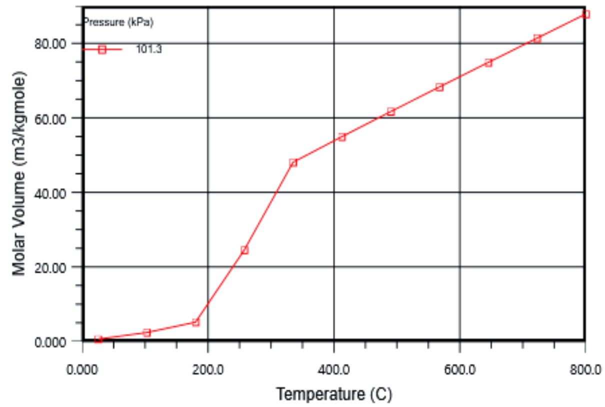
| | *Unit* | **cool** |
|---|---|---|
| | | |
| Heat Flow | *kJ/h* | 81251.32 |




Graph 1. Dependence of pyrolytic oil density on temperature.




Graph 2. Dependence of enthalpy of pyrolytic oil on temperature.




Graph 3. Dependence of molar volume of pyrolytic oil on temperature.

### 4.2. Process simulation using UNISIM Design

Table 4 The material balance of streams.

| Streams | *Unit* | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| *Parameters* | | | | | | | |
| *Vapour Fraction* | | 1 | 1 | 0 | 0.742 | 1 | 0 |
| *Temperature* | *C* | 320 | 450 | 450 | 200 | 200 | 200 |
| *Pressure* | *kPa* | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 |
| *Molar Flow* | *kmol/h* | 0.012 | 1.204 | 0.1 | 1.204 | 0.893 | 0.3099 |
| *Mass Flow* | *kg/h* | 100 | 98.8 | 1.201 | 98.80 | 37.96 | 60.84 |
| *Liquid Volume Flow* | *m3/h* | 0.106 | 0.154 | 7.3E-4 | 0.154 | 0.0757 | 7.9E-02 |
| *Heat Flow* | *kJ/h* | - 8.5E+4 | - 8.5E4 | 579.3 | - 1.8E5 | - 6.7E+04 | - 1.0E+05 |

The table above shows the simulation results of the thermal pyrolysis of HDPE. The conditions are the same as in the simulation in ASPEN HYSYS: 100 kg/h of food, temperature 450° C and the pressure is maintained at 1 atm. From pyrolysis, we get less than 1.5 kg/h of carbonic waste as the bottom stream and 98.8 kg/h of the top stream as steam sent to the condenser where pyrolytic oil and gases are separated. From the condenser we get 60.84 kg/h of pyrolytic oil from 86 kh/h that was predicted in the theoretical calculations.

The value is far from the calculated theoretical value. By comparing the final weights of the two simulation models, in

ASPEN HYSYS and UNISIM, we conclude that the most accurate results are achieved in ASPEN HYSYS, which has values that satisfy the thermal pyrolysis process of HDPE. This is because ASPEN HYSYS is the most advanced and specialised program for simulations, where we deal with polymeric and petrochemical components. Based on this conclusion, the economic evaluation was also carried out in ASPEN HYSYS V11.

### 4.3. Economic evaluation

| Table 4……(Summary) | |
|---|---|
| *Total Capital Cost [USD]* | 2,558,640 |
| *Total Operating Cost [USD/Year]* | 829,393 |
| *Total Raw Materials Cost [USD/Year]* | 4,274.19 |
| *Total Product Sales [USD/Year]* | 96,032.8 |
| *Total Utilities Cost [USD/Year]* | 31,237.8 |
| *Desired Rate of Return [Percent/'Year]* | 20 |
| *P.O.Period [Year]* | 0 |
| *Equipment Cost [USD]* | 16,500 |
| *Total Installation Cost [USD]* | 128,400 |

| Table 5…………(Utilities) | | | | | |
|---|---|---|---|---|---|
| Name | Fluid | Rate | Rate Units | Cost per Hour | Cost Units |
| Electricity | | 52.32 | KW | 4.0548 | USD/h |
| Cooling Water | Water | 0.000462 | MMGal/h | 0.05544 | USD/h |

$$\mathrm{NPV}(i,N)=\sum_{t=0}^{N}\frac{R_t}{(1+i)^t}$$

Initial investment=2,558,640$

$\boldsymbol{R\_t}$=**500.000**$

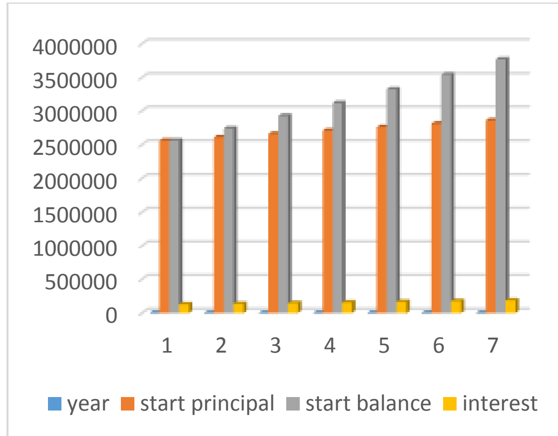
$\boldsymbol{i}$=**5**%

$\boldsymbol{t}$=**7** years

NPV=334,546.70$

Target = $2,000,000

We must contribute $196,544 at the end of each year to reach the goal. We would need an annualised rate of return of 5.642% to achieve the target. We must invest $1,132,043 at the beginning to achieve the target. We will have to invest 3,500 years to reach the target.




Graph 4 The results of the economic evaluation.

## 5. Conclusions

The end of this study is based on some basic theoretical knowledge of the behaviour of plastic polymers by temperature and the existence of different recycling methods. The chemical recycling of high-density polyethene was considered one of the most promising methods of recycling plastic waste. Today's most common plastic material, is polyethylene or polyethene (abbreviated PE; IUPAC name polyethene or poly(methylene)). It is a polymer mainly used for packaging (plastic bags, plastic films, geomembranes and containers including bottles, etc.). The chemical recycling method, also called pyrolysis, is one of the most efficient and effective methods of recycling waste plastic materials; simultaneously, it converts plastic waste into fuel. Pyrolysis is a sustainable waste management process and an environmentally friendly approach to treat solid plastic waste containing carbonaceous materials such as plastics and biomass. Thermal pyrolysis of high-density polyethylene waste was simulated in ASPEN HYSYS V11 and UNISIM. From the simulation results, we conclude that ASPEN HYSYS is an ideal simulator for this process, giving us a yield of 82.9%. Regarding the economic evaluation, the invested capital is returned after five to a maximum of seven years of operation.

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