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Investigation the Possibilities of Carbon Footprint Reduction of Steam Cracking by Using Hydrocarbons from Wastes

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Due to increasing in population and living standards, the demand for plastics has also grown dynamically over the past decades. The light olefins building the polymer chains can be produced in the largest quantities by steam cracking of hydrocarbons. In order to convert hydrocarbons into light olefins with the highest possible conversion, high temperatures and steam are required. Due to the high temperature, steam cracking emits large amounts of greenhouse gases into the atmosphere. In the interests of long-term sustainability and circular economy, the possibilities of CO_2 reduction obtained by steam cracking is in the focus. Mainly the suitability of new types of furnaces and heating systems are investigated. Due to the stricter environmental regulations petrochemical industry has to solve significant challenges. This includes the outstanding problem of recycling waste plastics. The aim of our research was to investigate the applicability of liquid hydrocarbons obtained from waste plastics in a steam cracking process. High olefin containing hydrocarbons were produced by low temperature pyrolysis from polymer wastes, then those hydrocarbon fractions were used as feedstock for steam cracking process.
Keywords: polymer waste, steam cracking, feasibility, CO_2 reduction, petrochemistry

1. Introduction

As the population and the living standards are higher each year, the demand for consumer plastics increased dramatically in the last decades. This demand is expected to grow even more in the coming decades. Every year more and more plastics especially polyolefins are produced (Chang, 2023; Geyer et al. (2017)). Because of these drives the light olefin production has a growing importance (Gholami et al. 2021; Kim et al. 2023; Precedence research, 2024a and 2024b). Steam cracking is the most significant technology in petrochemistry producing ethylene, propylene, and other olefins. The highest possible conversion can be achieved by this technology due to the high temperature and the right parameters applied. In the process high amount of steam used as well and involves a complex separation system also. To provide high temperature in the steam cracking furnace (min 800°C) it is necessary to use fuels with high heating values, e.g.: methane and other low carbon number hydrocarbons. The combustion of these can ensure the required energy meanwhile emits a lot of CO_2 and other greenhouse gases (Ebrahimi et al. 2023; Fakhroleslam and Sadrameli, 2019; Gholami et al. 2021; Mandviwala et al. 2024). It is a great challenge to minimize the negative effects of steam cracking. There are several ways to implement these ambitions, for example reducing the temperature of the furnace without the decrement of the ethylene and propylene yields. For this purpose, it is crucial to investigate the effect of different kind of raw materials. The composition and other physical properties e.g.: density, viscosity and boiling point range of the raw material are key factors in the process of steam cracking (Fakhroleslam and Sadrameli, 2019; Gholami et al. 2021). Another important parameter is the steam/hydrocarbon ratio. Regarding the application of dilution steam, the reduction of coke formation is also important in the investigations of the optimization of steam cracking technologies (Fakhroleslam and Sadrameli, 2019; Gholami et al. 2021; Song and Tang, 2018). New types of furnaces and heating systems also can be investigated in terms of energy efficiency and to minimize the carbon footprint of the technology (Mandviwala et al. 2024; Ebrahimi et al. 2023).
The feedstock of conventional steam cracking comes from crude oil refineries. In the European Union (EU) there is a great effort to minimize the consumption of fossil originated raw materials. Meanwhile the amount of plastic

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waste is larger every year, which is rich in carbon and hydrogen. These can be recovered from plastic waste with appropriate processes, which can promote the directives of EU, to implement the circular economy. There are several investigations to use plastic waste as raw material to generate blending components for transportation fuels or to use in petrochemistry. It can be carried out by the thermo-chemical conversion of plastic waste (Mandviwala et al. 2024; Nabgan et al. 2023; Nixon et al. 2024; Sharuddin et al. 2016; Tejaswini et al. 2022). Thermo-chemical processes including pyrolysis and gasification mainly. As a result, the macromolecules of polymers are cracked into lower carbon number hydrocarbons. It results gaseous and liquid products and solid residue in the cases when the degradation reactions are not fully completed (Sharuddin et al. 2016; Tan et al. 2023; Tejaswini et al. 2022). Applying high surface catalysts during these processes can lower the activation energy and increase the quality of the obtained products (Sharuddin et al. 2016; Tan et al. 2023). In the case of steam cracking there is also an opportunity to use waste-sourced raw materials. The pyrolysis oil from plastic waste can be a feedstock to steam cracking. By achieving this value chain, virgin quality polyolefin could be produced from plastic waste. This would be beneficial not only for waste recycling, but also to serve the growing demand for plastics (Mandviwala et al. 2024). The economic aspect of the steam cracking process has great importance especially in the case of plastic waste sourced liquid fractions. Optimization of steam cracking means to lower the temperature and maintain a high yield of low carbon number unsaturated hydrocarbons. In addition, the cost and physical properties of the raw material have a great impact on the optimization as well. These parameters can minimize the operational costs. To minimize the capital costs of new plants needs further investigations, e.g.: furnace configuration, energy integration, optimization of transfer line exchanger (TLE) etc (Song and Tang, 2018). Figure 1 shows the connection between the raw materials, process plants, and products. This processing chain can promote a circular economy.

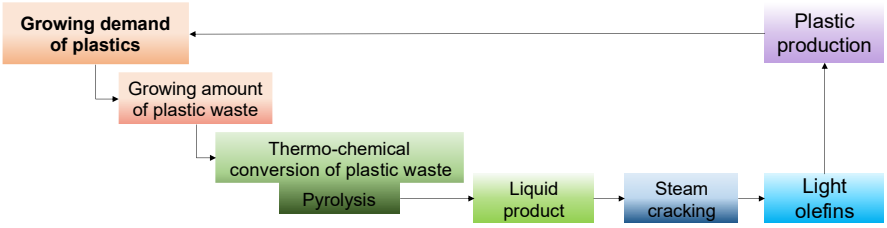

Figure 1: Structure of plastic waste-based steam cracking process to produce plastics (based on Mandviwala et al. 2024)

In our work gasoline and gas oil fraction hydrocarbons were investigated in a laboratory scale single-pass steam cracking furnace. As reference, straight run Gasoline and Gas oil were investigated first. The liquid product of polyethylene (PE) pyrolysis was distilled to gasoline and gas oil fraction, and these were investigated as waste source raw materials of steam cracking. Before the experiments the physical properties and composition of the raw materials were determined. The gaseous product of the steam cracking was analyzed. This laboratory-scale experiments are preliminary experiments for a larger-scale steam cracking unit.

2. Materials and methods

2.1 Raw material

As reference standard quality Gasoline and Gas oil were investigated first in the steam cracking reactor. The properties of these liquids were determined before the experiments, it is described in Section 2.2. As a waste source feedstock for steam cracking reactions the liquid product of polyethylene pyrolysis was used. The pyrolysis of the polyethylene was carried out in a continuous tube reactor at 450°C. The pyrolysis oil was distilled to gasoline and gas oil fraction manually at atmospheric pressure. The physical properties of the pyrolysis oil-based gasoline and gas oil fraction were also determined. For the steam cracking investigation, a laboratory scale custom-made steel tube was used in a Carbolite Gero Furnace. The tube had three inlets on the top and one outlet tube on the bottom. The inlet tubes were connected in the first half of the tube. The furnace was vertically configured. Raw materials were introduced on the top of the tube and the products left the reactor at the bottom. To carry out the steam cracking reaction in addition to the hydrocarbon feedstock, water and nitrogen gas were also introduced. The steam/hydrocarbon ratio was 0.8g steam/1g hydrocarbon in all cases. 2L/h nitrogen gas was used in the experiments as a carrier gas and to ensure the inert atmosphere. The hydrocarbon, water, and nitrogen gas were introduced separately on the three inlet tubes. In the middle tube the nitrogen was introduced, its internal diameter was 6mm. On the two side tubes the hydrocarbon raw material and water were introduced, these tube's internal diameter was 3.7mm each. The liquid raw materials were introduced with DG series Leadfluid Peristaltic Pumps. In the steam cracking experiments in all cases the hydrocarbons were introduced with 25g/h and the water was introduced 20g/h mass flow. The experiments were carried out at 800,

850 and 900°C. The liquid product was condensed into a borosilicate bottle, the non-condensable gases were collected in a Tedlar-type gas bag. Figure 2 shows the layout of the main parts of the steam cracking furnace and the product separation and collection. The gaseous products were analyzed by gas-chromatograph.

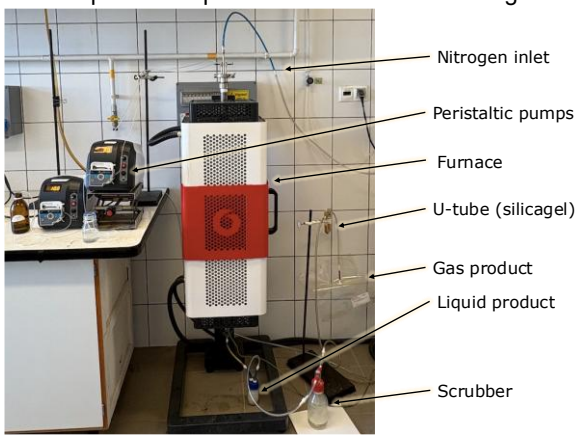

Figure 2: The layout of the laboratory scale steam cracking process

2.2 Analysis

The density and viscosity of the raw materials were measured by an Anton Paar SVM 3000 type Stabinger Viscometer at 20°C. The boiling point range of the liquids were determined by a PAC Mini method type equipment by ASTM D7345 micro distillation standard test. The composition of the raw materials were determined by a Shimadzu QP2020 gas chromatography/mass spectrometry (GC-MS) equipped with TIC detector. The temperature of the injector was at 300°C, the interface was at 280°C, the ion-source was at 200°C. The column was an SHI-1 MS type (30m long with an internal diameter of 0.25mm and film thickness of 0.25µm). The temperature of the column was at 40°C for 5 minutes then it was elevated at 330°C with a heating rate of 10°C/min. The temperature was hold at the final temperature for 5 minutes. The mass spectrometry was in Scan mode, the event time was 0.03sec, m/z was between 35 and 400. The evaluation of the chromatograms was made by Real Time Analysis software and MS Excel. The obtained gas products were analyzed by a DANI gas-chromatograph (GC) equipped with TCD, and FID detectors. The hydrogen and methane content of the gas products were determined by GC-TCD method, and the volatile hydrocarbon content from methane up to C_5 components were determined by GC-FID method. The temperature of the injectors was 100°C, the detectors were at 210 °C. The used columns were an Rtx-1 PONA type (100m long with an internal diameter of 0.25mm and film thickness of 0.5µm) in the case of TCD detector, and a Carboxen™ 1006 PLOT column (30m long and 0.53mm internal diameter) in the case of FID detector. The columns were at 35°C for 13 minutes at the beginning of the measurements, then the temperature was elevated at 100°C with a heating rate of 5°C/min. The final temperature was maintained for 2 minutes. The evaluation of the chromatograms was made by Clarity7.4 software and MS Excel.

3. Results and discussion

3.1 Properties of the raw material

The distillation curves of the hydrocarbon raw material can be seen on Figure 3. Looking at the results in the case of gasoline and gas oil fraction the PE based liquid is more volatile than the straight run fuels.

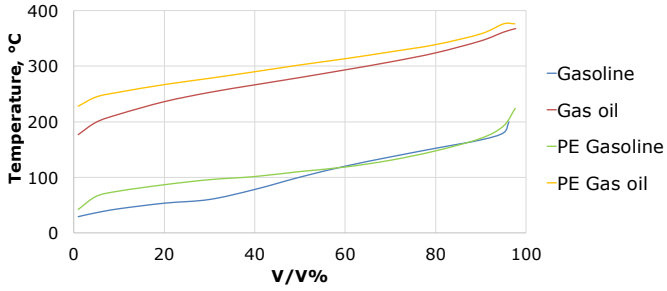

Figure 3: The distillation curves of the liquid raw materials for steam cracking

The density and viscosity results can be seen in Table 1. The properties of the straight run fuels and the polyethylene sourced fractions are similar to each other.

Table 1: The density and kinematic viscosity of the liquid raw materials for steam cracking

	Density, g/cm^3	Kinematic viscosity @20°C, mm^2/sec
Gasoline (straight run)	0.749	0.36
Gas oil (straight run)	0.833	4.87
PE Gasoline	0.754	0.28
PE Gas oil	0.797	5.46

In spite of the similarities, the composition of the straight run fuels and the PE sourced liquids are different. Figure 4 shows the composition of the 4 raw materials. In the case of straight run Gasoline, isomers and aromatics took a major part of the composition. Meanwhile the PE-based Gasoline fraction contains mainly olefins and paraffins. Differences can also be observed comparing the straight run Gas oil and PE sourced Gas oil. The latter has a higher concentration of dienes meanwhile the conventional Gas oil has a higher paraffin content. These can influence the yield of the obtained products and the composition of the gas product of the steam cracking experiments.

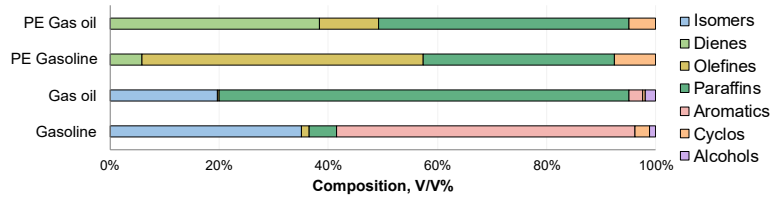

Figure 4: The distillation curves of the liquid raw materials for steam cracking

3.2 Product yields

During the steam cracking process gaseous and liquid product was obtained as well. To determine the product yields in weight%, the introduced weight of the raw materials was calculated from their mass flow and the duration time of the experiment. The weight of the liquid products was measured at the end of the experiments. From these, the product yields could be calculated, and the results can be seen in Figure 5. Increasing the temperature causes higher gas yields and lower liquid yields except in the case of standard quality Gas oil, in those yields cannot be seen significant difference. The highest gaseous product yields were obtained in the case of PE Gasoline raw material, especially at 900°C (~93wt%). The liquid products of the experiments had two phases, an oily rich phase, and an aqueous phase. Most of the liquid products were in the aqueous phase, with only a small amount of organic phase on top.

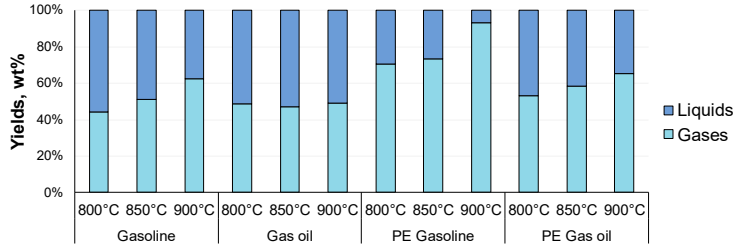

Figure 5: The product yields from steam cracking in wt%

3.3 Gas compositions

The components in gas products are summarized in Figure 6. The gas composition can give information about the efficiency of the steam cracking process. The most relevant product of the process is ethylene, but hydrogen and other hydrocarbons also appeared in the gas products as well. It can be seen when the temperature was higher the ratio of hydrogen and shorter hydrocarbons in the gas products are higher. The highest hydrogen (H2) content was obtained in the case of PE Gasoline at 900°C (~33V/V%). Increasing the temperature causes the highest increment in the hydrogen content in the case PE Gasoline. The hydrogen content of the gas product is higher in the cases of PE Gasoline and PE Gas oil raw material than standard fuels. It can be explained by the higher volatile content of the Methane (CH_4) content of the gas product was higher in the cases of standard fuels than in the cases of PE based liquids. The highest methane content was obtained in the case of straight run Gasoline at 900°C (~24V/V%). It can be also seen that the increment in methane content with the

temperature rising is significantly higher in the cases of straight run Gasoline and Gas oil than in the cases of PE Gasoline and PE Gas oil raw material. The straight run fuels, especially straight run Gasoline, contain more isomers which can be converted to methane during the steam cracking reactions (Figure 4).

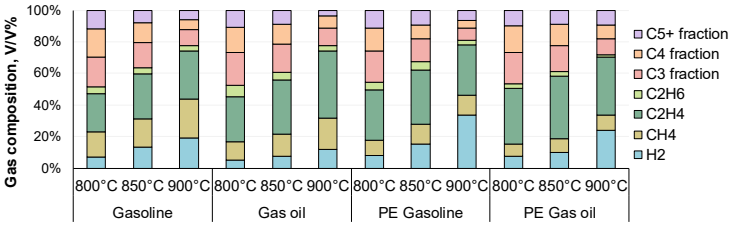

Figure 6: Gas composition of the gaseous products in V/V%

In the ethylene (C_2H_4) content similar trends can be seen in the terms of rising the temperature. The highest ethylene content was obtained in the case of straight run Gas oil raw material at 900 °C (~42V/V%). Although at 850°C the highest ethylene content was obtained in the case of PE Gas oil (~39V/V%). At 800°C similar phenomena can be seen. The PE based raw materials had higher olefin content which can be more easily converted to low carbon number olefins such as ethylene in a steam cracking unit (Figure 4). The ethane (C_2H_6) content of the gas product was less significant than the ethylene content, but it is very important also. Higher carbon number volatile hydrocarbons were also appeared in the gas product up to C_5 components. The obtained volume of these components is less at higher temperatures. From these components the C_3 fraction was the most significant. For all raw materials there is not significant difference in the obtained volume of C_3 fraction. The C_4 fraction contains saturated and unsaturated hydrocarbons in isomer and normal form as well. The C_4 fraction of the gas product is less than 20V/V% in each case, and at 900°C it is less than 10V/V%. The C_{5+} fractions make up around 10V/V% of the whole gas maximum.The obtained amount of the components was calculated to mmol to eliminate the differences. It was calculated by the product yields, Volume% of the gases and the molar weights (in the case of fractions average molar weights). The results show how much mmol of the components were produced from one mass unit of raw material (1g). The results can be seen in Figure 6a. The hydrogen yield is much higher than the other components, for readability reasons Figure 6b shows the results without hydrogen.

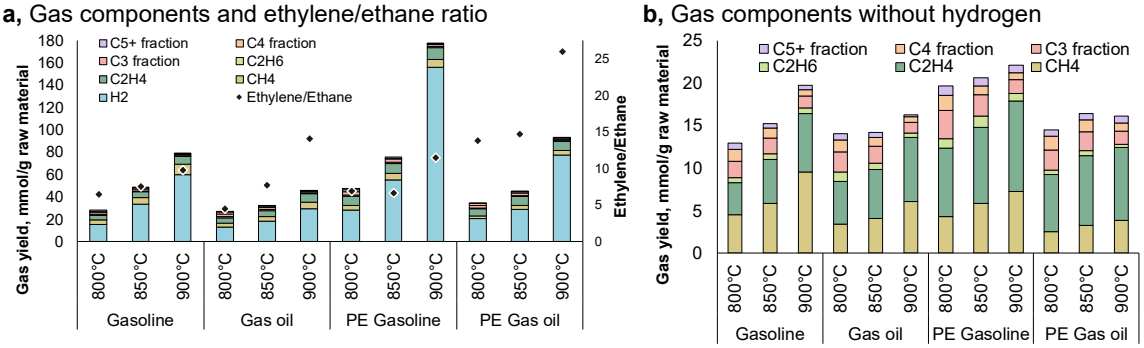

Figure 6: The yield of the gas components in mmol/g raw material

From these results similar trends can be seen as in the gas compositions. However, based on the different conversions and product yields, in these results great differences can be seen between the raw materials and temperatures. The highest amount of gas components was obtained in the case of PE Gasoline raw material at 900°C. The hydrogen content of the gas products is the most significant (156mmol/g raw material). In general, it can be seen, that in the case of PE based liquids higher amount of hydrogen was produced, especially in the case of PE Gasoline at 900°C. In the methane content the lowest amount of it was obtained, in the case of PE Gas oil at 800°C (2.5mmol/g raw material) and the highest amount was obtained in the case of straight run Gasoline at 900°C (9.5mmol/g raw material). In addition, the ethylene content is also significant in the gas product. The highest ethylene yield was 10.6mmol from 1g raw material in the case of PE Gasoline at 900°C. At 800°C in the case of PE Gasoline the produced amount of ethylene was 8.0mmol from 1g raw material, while in the case of straight run fuels the maximum yield of it was 7.5mmol/g raw material at 900°C in the case of Gas oil. The obtained amount of ethane was significantly lower than ethylene. It is worth to mention the ratio of the produced amount of ethylene and ethane increasing with temperature. The highest ethylene/ethane ratio was obtained in the case of PE Gas oil at 900°C. Furthermore, in the case of PE Gas oil at 800°C and 850°C similar ethylene/ethane ratio was obtained as in the case of straight run Gas oil at 900°C. In the case of straight run Gasoline and PE Gasoline similar ratios were obtained at the same temperatures.

4. Conclusions

In this decade, finding solutions to reduce the amount of plastic waste in a sustainable way is inevitable. Also, it can be stated that the required amount of plastic products is higher each year. To connect these drives by the thermo-chemical conversion (pyrolysis) of plastic waste and to use the obtained hydrocarbon rich liquid product as a raw material for steam cracking could be beneficial at many levels. In our experimental work we would like to investigate the potential of this process. For this purpose, we made steam cracking experiments at 800-, 850- and 900°C with standard fuels and with plastic waste (PE) sourced hydrocarbon fractions as well. From the results at 800°C using PE Gasoline higher gas yield can be achieved than straight run Gasoline at 900°C (respectively 62.5wt% and 93.0wt%). In terms of ethylene production in steam cracking reactions, the highest concentration was obtained by straight run Gas oil raw material at 900°C (42.7V/V%). However, at 850°C by PE Gas oil raw material can be generated the highest concentration of ethylene (39.4V/V%). Based on product yields, gas compositions and molecular weights the obtained amount of components in mmol from 1g raw material was calculated. From these results it can be also seen that the plastic waste sourced raw materials are beneficial in ethylene production. PE Gasoline could generate higher amount of ethylene at 800°C than straight run Gasoline at 900°C (respectively 8mmol/g raw material and 6.9mmol/g raw material). The results of our experiments are promising, although further investigations are needed to explore the topic in greater detail, including scale-up experiments and calculations.

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