Supplementary Information

## Mechanistic Insights into the Thermal Pyrolysis of High-density Polyethylene and Polypropylene: Towards Sustainable Hydrogen Production and Carbon Valorization

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### Argon flow rate variation

Initially, different argon flow rates were tested during HDPE pyrolysis to determine the optimal gas flow for subsequent experiments. For this purpose, the temperature was set at 1000 °C, and the argon flow rate was varied from 100 to 700 ml min$^{-1}$. The resulting gas-phase was analyzed via GC, and the results are presented in Figure S1. It is evident that the flow rate of the inert gas has only a minor influence on the gas-phase results. An argon flow of 175 ml min$^{-1}$, which provides a residence time of 10 s at 1000 °C, was chosen to balance adequate dilution with sufficient reaction times. To keep the residence time at 10 s when setting other temperatures, the argon flow was changed accordingly, as can be seen in Table S3.
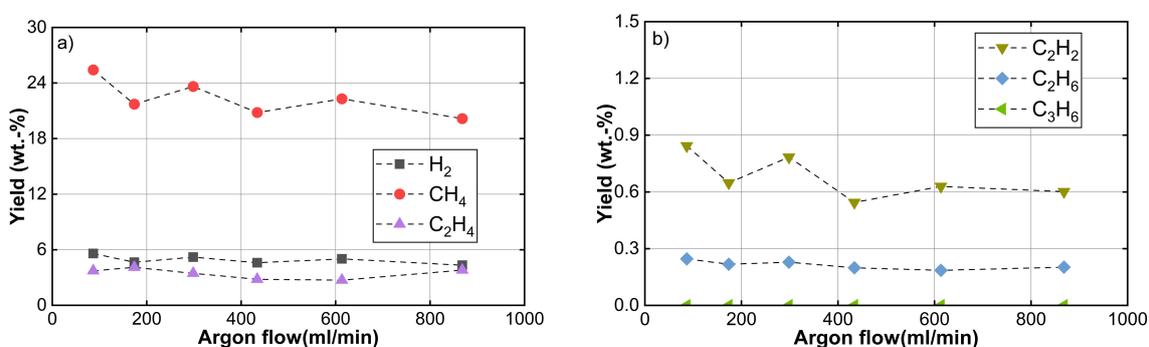


**Figure S1.** Results of the gas-phase components of the HDPE pyrolysis at 1000 °C at different argon flow rates. To keep the conduction of the experiments consistent, the flow rate of 175 ml min$^{-1}$ was maintained for all pyrolysis experiments in this work.
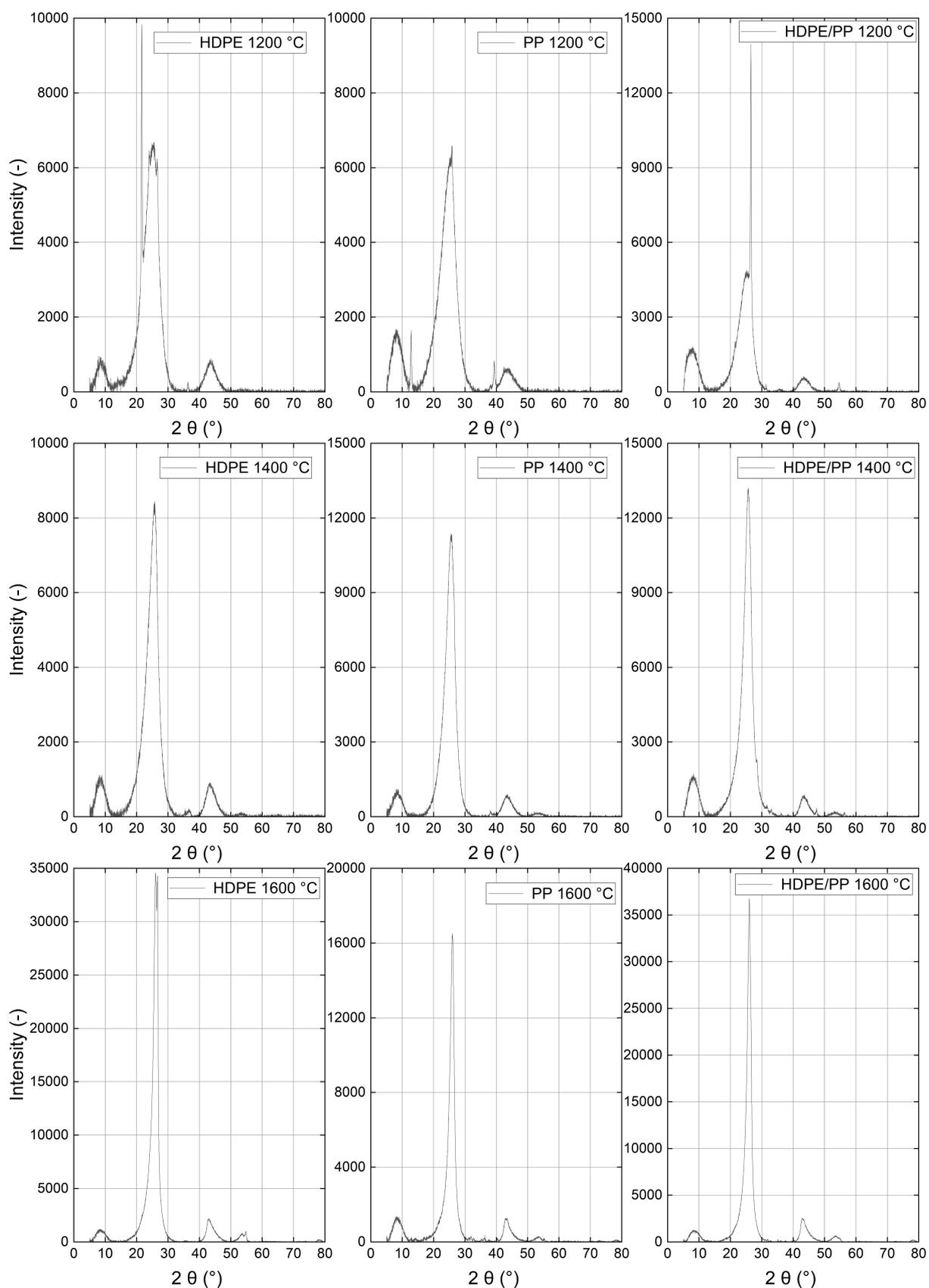
## X-ray diffraction patterns



**Figure S2.** XRD patterns of HDPE, PP, and HDPE/PP samples.
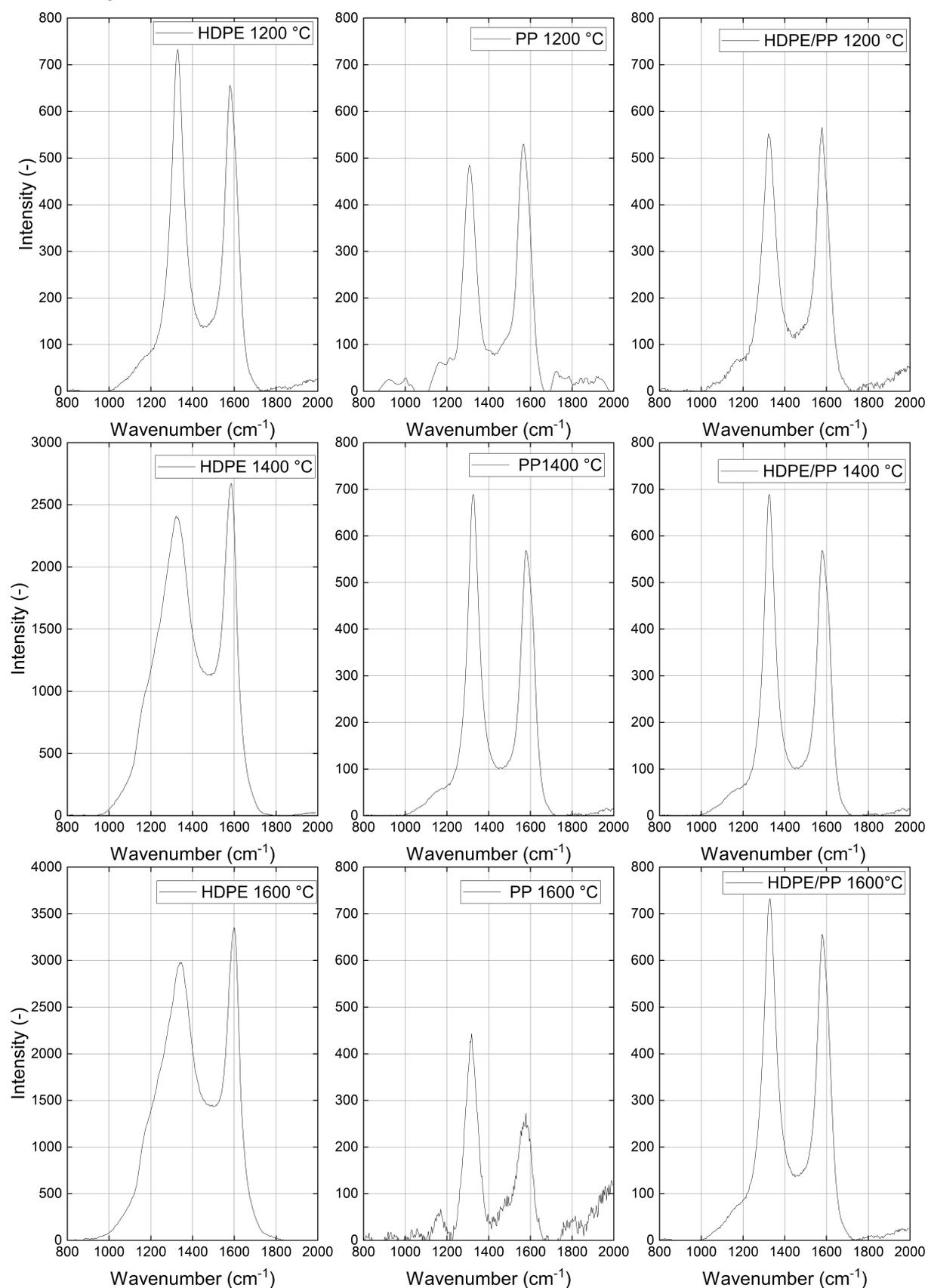
## Raman spectra



**Figure S3.** Raman spectra of HDPE, PP, and HDPE/PP samples.

# Supplementary Information

## GC analysis of the liquid sample

**Table S1.** Aliphatics chain length distribution for HDPE, PP, and HDEP/PP samples.

| Aliphatics: Chain length distribution | | | | Samples: HDPE, PP, HDPE/PP | |
|---|---|---|---|---|---|
| RT-Window | Chain length | Calibration Factor | Area | Concentration | Percentage |
| 6.05-10.10 | C12-15 | 16 | 0.1186 | 1.944 | 1.1 |
| 10.15-16.20 | C16-20 | 31 | 0.0532 | 1.640 | 0.9 |
| 16.25-21.50 | C21-25 | 66 | 0.0817 | 5.369 | 3.0 |
| 21.55-25.80 | C26-30 | 176 | 0.0683 | 12.021 | 6.6 |
| 25.85-29.40 | C31-35 | 2846 | 0.0562 | 159.934 | 88.4 |
| 29.45-32.00 | C36-40 | 13422 | 0.0000 | 0.000 | 0.0 |
| | | | Sum | 180.909 | 100.0 |

The aliphatic compounds are divided based on their retention times or carbon number groups as specified in the table. The peak areas are evaluated within their respective retention time windows and partial totals are recorded in the corresponding cells of the table. This will provide the concentration in µg mL$^{-1}$ for each carbon number group, as well as the total concentration of aliphatic compounds within the aliphatic fraction. The "Percentage" column indicates the relative distribution of the carbon number groups in the aliphatic fraction.

Note: The retention time (RT) windows and calibration factors may vary with each calibration.

**Table S2.** PAHs distribution for HDPE, PP, and HDEP/PP samples.

| PAHs-Distribution | | | | Samples: HDPE, PP, HDPE/PP | |
|---|---|---|---|---|---|
| RT-Window | Chain length | Calibration Factor | Area | Concentration | Percentage |
| 5.50-10.50 | 2-Ring | 4.7952 | 0.11 | 0.510 | 9.2 |
| 10.51-16.40 | 3-Ring | 5.1536 | 0.54 | 2.803 | 50.5 |
| 16.45-24.1 | 4-Ring | 4.9791 | 0.36 | 1.790 | 32.2 |
| 24.15-27.70 | 5-Ring | 5.4041 | 0.08 | 0.452 | 8.1 |
| 27.75-30 | 6-Ring | 5.3683 | 0.00 | 0.000 | 0.0 |
| | | | Sum | 5.555 | 100.0 |

PAHs are divided according to their retention times or the number of 6-membered rings, as detailed in the table. The peak areas are calculated within the specified retention time windows, and these partial sums are then entered into the corresponding cells of the table. This will yield the concentration in µg mL$^{-1}$ for each PAHs group, with their total representing the overall concentration of aromatics and PAHs in the aromatic fraction. The "Percentage" column shows the relative distribution of each PAHs group among the aromatics.

Note: The retention time (RT) windows and calibration factors may differ with each calibration.

## Argon flow rate for a residence time of 10 s

**Table S3.** Argon flow rate set to provide a residence time of 10 s in the isothermal hot zone.

| Temperature / °C | Argon flow rate / ml min$^{-1}$ |
|---|---|
| 700 | 227.13 |
| 800 | 205.96 |
| 900 | 188.41 |
| 1000 | 173.61 |
| 1100 | 160.97 |
| 1200 | 150.04 |
| 1300 | 142.90 |
| 1400 | 132.10 |
| 1500 | 124.65 |
| 1600 | 118.00 |

## Influence of temperature on the gaseous-product composition

The pyrolysis of HDPE, PP, and their 1:1 mixture was investigated over a temperature range of 800–1600 °C. The mass distribution was quantified as gas and solid+liquid fractions (sum = 100%), which is summarized in Figure S4. For HDPE, the maximum gas yield was observed already at 800 °C, whereas PP reached its peak gas production at 1200 °C. The HDPE/PP mixture exhibited the highest gas yield at around 800 °C. Beyond these temperatures, the gas fraction for all samples gradually decreased, reaching approximately 10% at the highest temperatures. The data point to a shift from a high share of gas phase products at lower temperatures to increasing relevance of liquid and solid products with rising temperature.
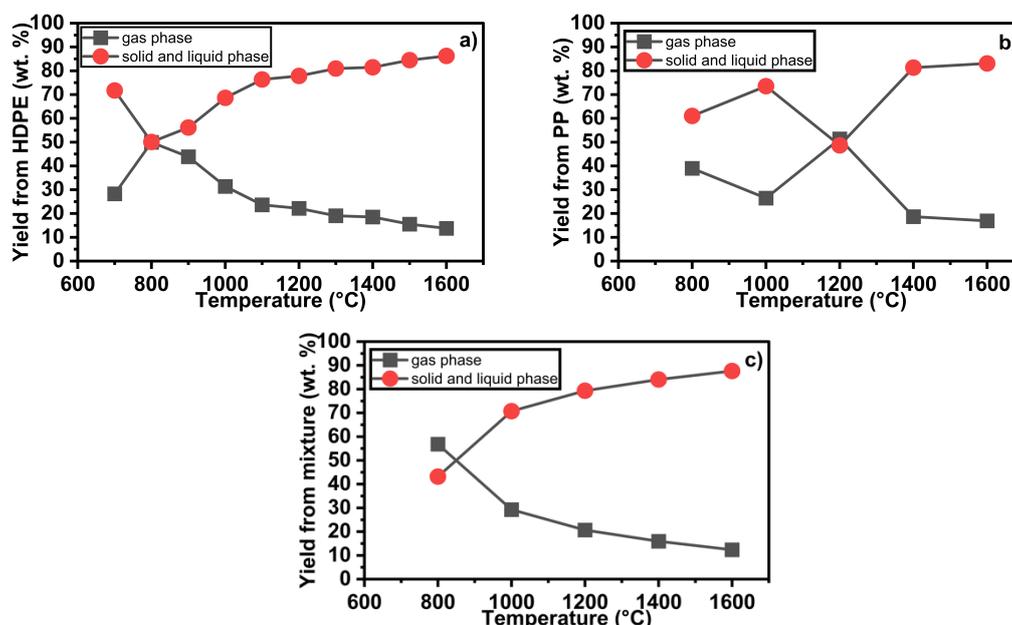
**Figure S4.** Temperature influence on the distribution of mass-related product yields regarding gas phase versus solid and liquid phase for pyrolysis experiments with HDPE (a), PP (b), and 1:1 HDPE/PP mixture (c).

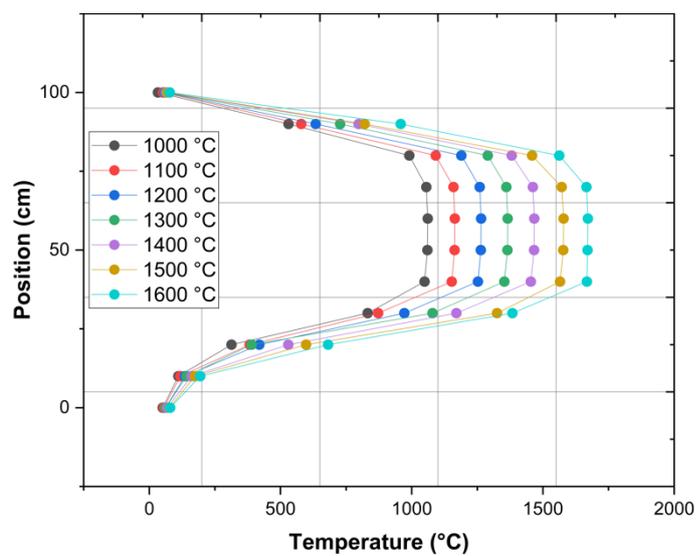## Temperature profile of the reactor used in this study



**Figure S5.** Axially resolved temperature profile in the reactor for temperatures ranging from 1000 to 1600 °C (residence time of argon: τ = 10 s).

## Individual yields of the product species for every polymer

Figure S6 shows the yields for the individual product species (a-f) for HDPE, PP, the average calculated value from the yield of HDPE and PP combined (weighed 1:1) and the resulting measured yield from the mixture. The results of the mixture mostly lie between those of the individual polymers; however, PP seems to have a somewhat larger influence on the gas phase composition at high temperatures than HDPE. That the pyrolysis behavior of the mixture is influenced by interactions between intermediate decomposition species from both polymers is discussed in greater detail in the context of liquid phase analysis (see main manuscript).
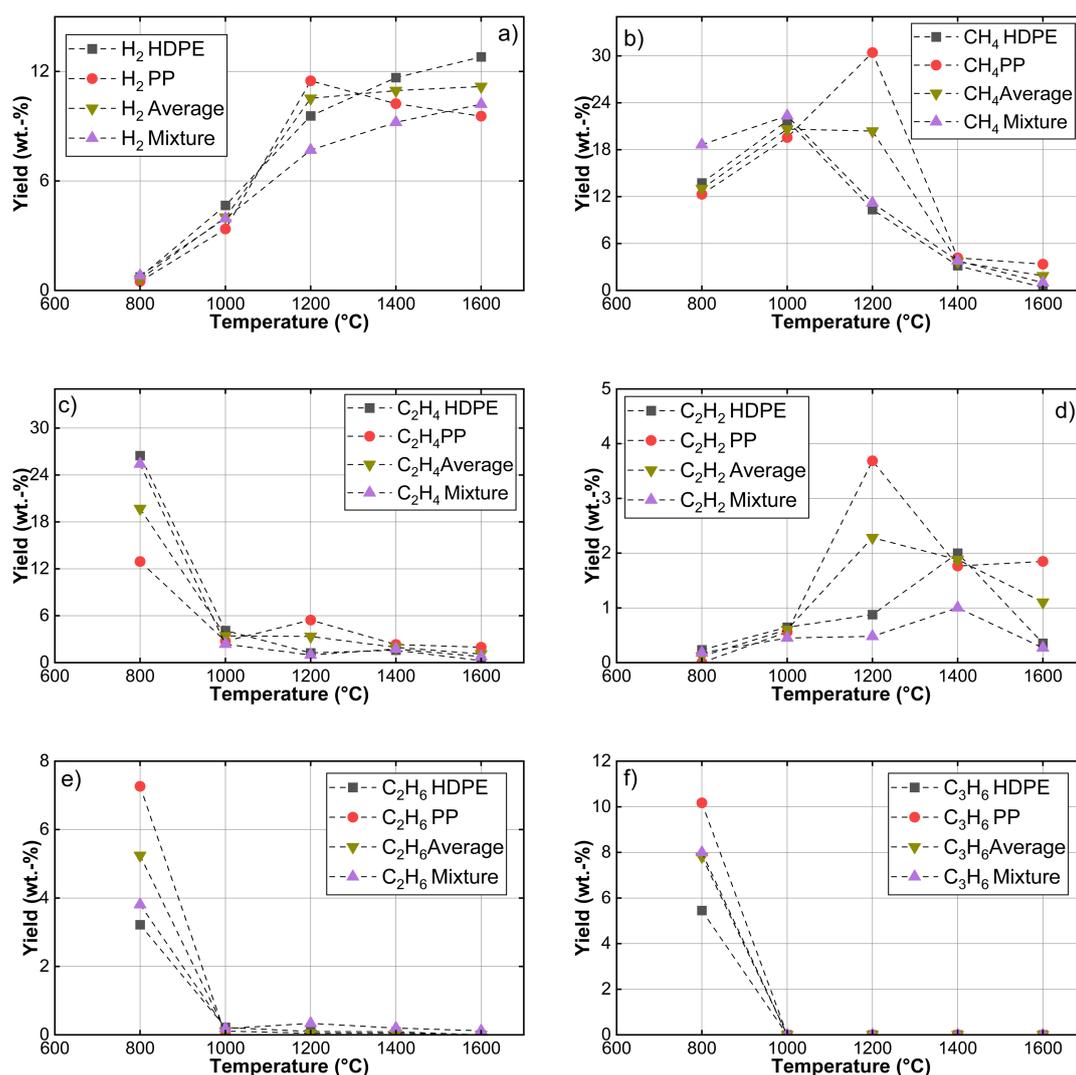


**Figure S6.** Yields of the individual polymers, the average yield from both polymers (weighed 1:1) for every temperature, and the yield measured for the mixture for every species illustrated in the separate Figures a)-f).