



Thermal and catalytic co-pyrolysis of pure and waste High Density Polyethylene with Vacuum Gas Oil

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Motivation

The world production of plastics has been increasing at a high rate, having negatively impacted the consumption of fossil carbon and problems such as the accumulation of plastic waste and global warming (Plastics Europe, pp.1-42, 2019).

The promotion of tertiary recycling was identified to be a viable way to minimize those problems and to optimize the current management of plastic waste, as there are significant amounts of plastics, that have enough quality to undergo this type of recycling but instead are incinerated or sent to landfills (P. Lettieri and J. Baeyens, Waste Manag., vol. 29, pp. 2625–2643, 2009). Associated to an instability in the fuel market and the origin of most plastics, an attractive alternative of valuing them is through their direct incorporation into the Fluid Catalytic Cracking (FCC) unit, having this several advantages, such as being a simultaneous purification/upgrading process that can value a wide range of raw materials in large quantities.

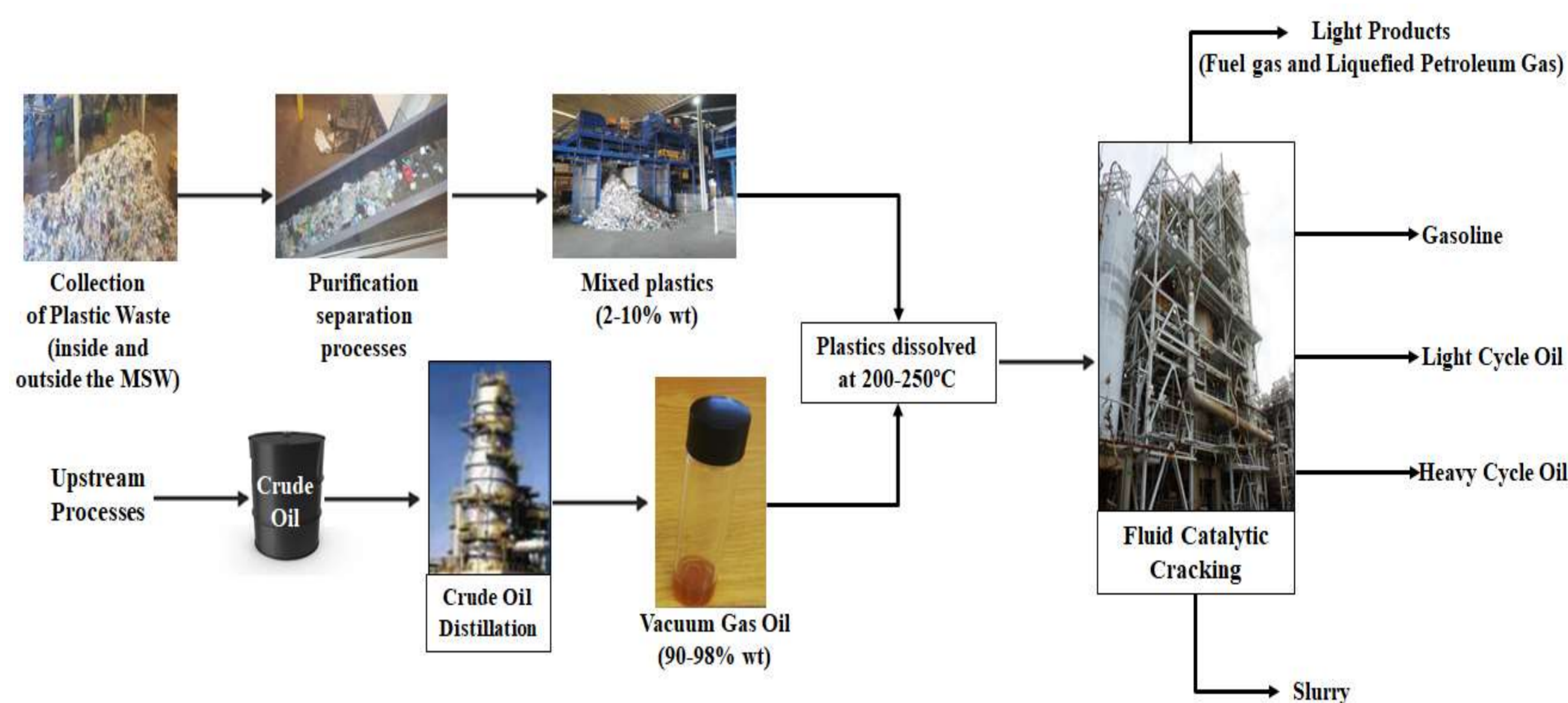


Figure 1- Proposed scheme of the incorporation of plastic waste into the FCC unit.

However, as research is still at an early stage, this work focused on the thermal and catalytic pyrolysis process of one of the most common type of plastic waste, high density polyethylene (HDPE), in co-processing with vacuum gas oil (VGO), in order to evaluate the feasibility of co-processing plastic with a typical FCC feed (Figure 1).

Results

Experiments using different VGO-polymer (waste HDPE obtained from shampoo bottles and pure HDPE provided by Repsol) mass ratios were carried-out in a simultaneous thermal analyzer (DSC-TG) and in a semi-batch bench-scale reactor, as these are the first stages of an efficient scale up process.

DSC-TG

Experiments were performed, using the following procedure:

20 mg of sample and 40 mg of Equilibrium FCC catalyst (for catalytic experiments) were introduced in an alumina pan, which was inserted into the DSC-TG. In this, an inert atmosphere was ensured by a nitrogen flow of 20 ml/min, which was also used to purge the equipment before the start of the run; The run temperature was stabilized at 40 °C for 10 minutes and then heated at 10°C/min, up to 700°C, where it was maintained for 10 minutes, before cooling.

Blank experiments with empty pans were used to establish adequate DSC baselines. In addition, thermal and catalytic experiments were carried out with different HDPE mass incorporations (0%, 10%, 20%, 50%, 80%, 100%).

Some of the results are depicted graphically in Figure 2.

Semi-batch reactor

In a typical run, around 5 g of the reactants were introduced into a Schlenk-type glass vessel of 0.1 dm³, together with 10 g of catalyst for the catalytic transformation experiments. The reactor was placed in an oven and connected to a liquid collection system, topped by a condenser cooled by water at 20 °C. The outlet of the condenser was connected to a gas burette. The system was filled with nitrogen and the reactor was heated, at a rate of 10 °C/min, up to 500°C, which was kept for 90 minutes (E. Santos et al., Catalysis Today, vol. 379, pp. 212–221, 2021).

The temperature profile inside the reactor was measured continuously and the reaction products (heavy mixture, coke, liquid and gas) were separated, being the liquid and gas products analysed by gas-chromatography, while the remaining products were characterized by DSC-TGA. 4 experiments were carried out with different HDPE mass incorporations (0%, 10%, 50%, 100%), being some of the results represented in Figure 3.

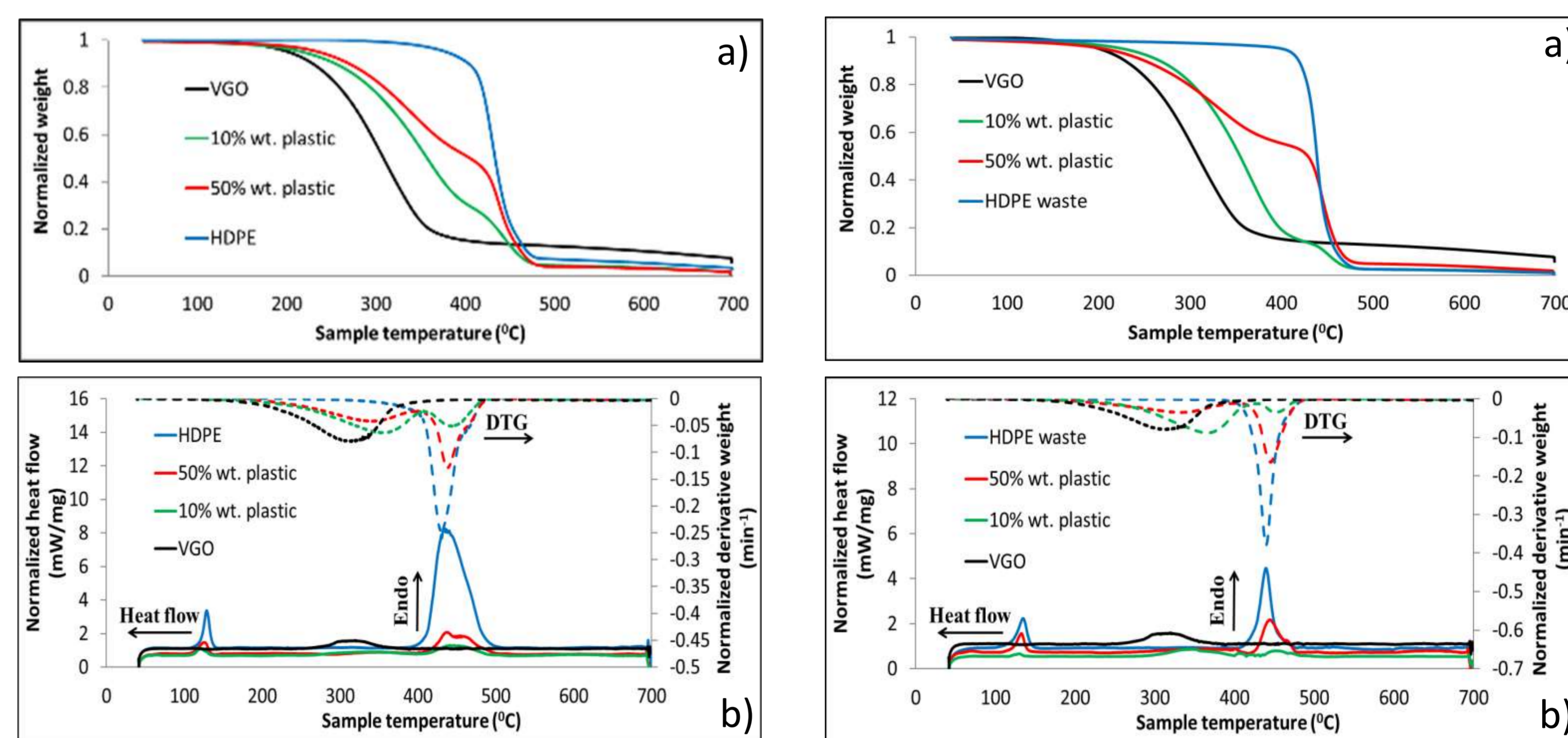


Figure 2- Catalytic co-processing between HDPE type plastics and VGO. a) Normalized weight loss. b) Normalized derivative weight and heat flow.

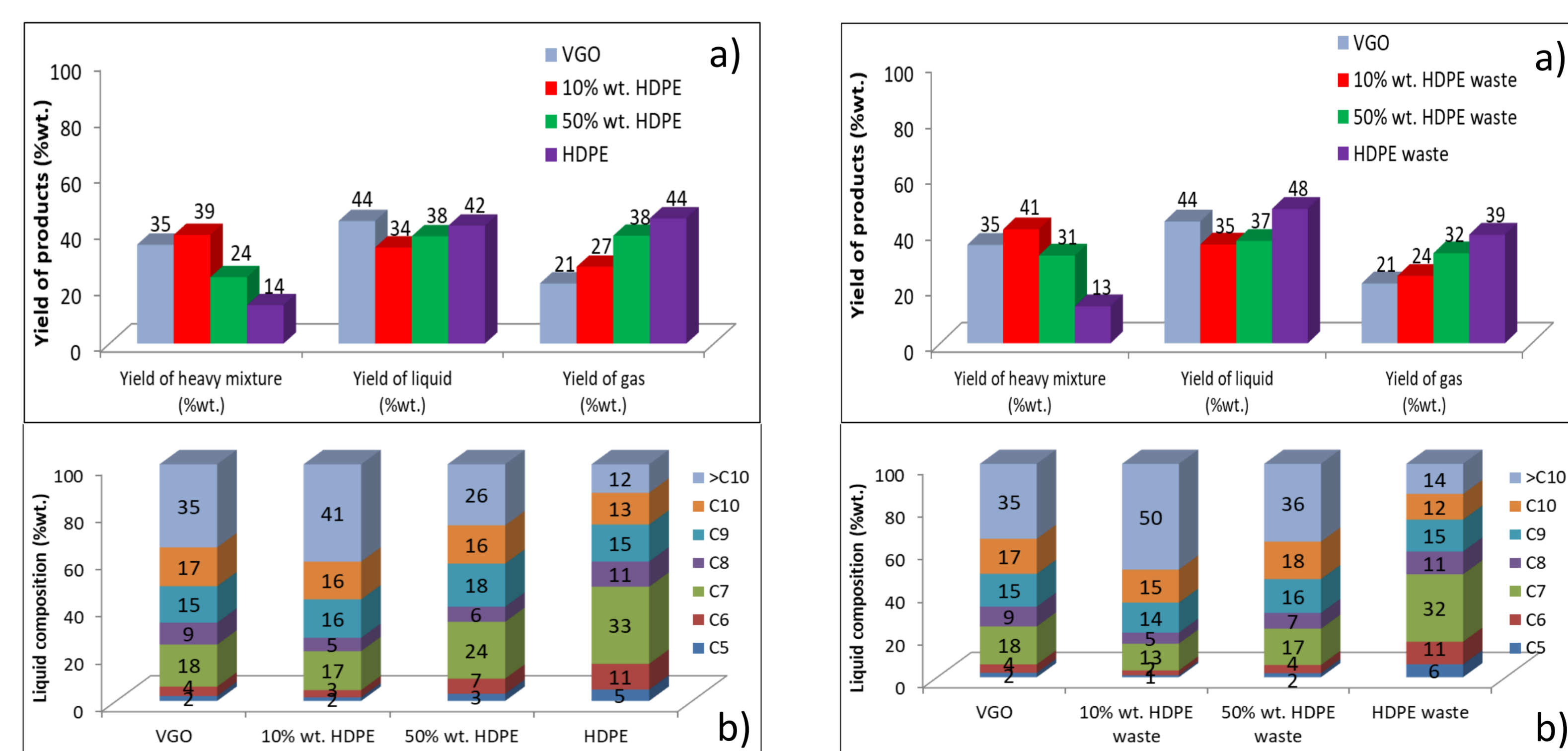


Figure 3- Catalytic co-processing between HDPE type plastics and VGO. a) Yield of products. b) Composition of the liquid products.

Main conclusions:

- Compared to VGO, HDPE loses mass at higher temperatures and needs more energy to degrade, while producing a larger quantity of lighter and higher value products;
- Waste and pure HDPE don't appear to possess many significant differences between each other when analyzed individually or mixed with VGO;
- The limited incorporation of HDPE type plastics in an FCC feed can be successfully carried-out within regular refining conditions, as this doesn't seem to negatively impact the process or the resulting products, with this corresponding in a worst-case scenario to a weight-by-weight replacement of VGO by a mostly negative value material which is highly available, making this, a viable way to recycle plastic waste in the future.