# Study of the decomposition of Vacuum Gas Oils-Low Density Polyethylene blends: evolution of the gases



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**ABSTRACT**

Plastics have been one of the materials with the fastest growth because of their wide range of applications: packaging, agriculture, construction, household, etc.

Pyrolysis is a tertiary recycling process, where the polymer sample is heated in an inert atmosphere causing the cracking of the polymer backbone. In the catalytic pyrolysis, the catalyst causes an important reduction in the decomposition temperature and allows more valuable gaseous products to be obtained.

In this work, dynamic pyrolysis of different samples of vacuum gas oil (VGO), polyethylene (PE) and a vacuum gas oil-polyethylene blend with 10% PE (VGO-PE) have been performed in a vertical reactor in order to study the thermal and the catalytic pyrolysis using an equilibrium FCC catalyst. Different to most of the works studying the composition of the products evolved in the pyrolysis process, which analyzes the overall gaseous or liquid product collected through the complete degradation of a given polymer, in this case, the evolution with the temperature (or the time) of the composition of the gases evolved has been studied by GC/MS. The results obtained permit the nature of the processes involved in each step of decomposition to be better understood and to analyze the possibility of recycling plastics by mixing them with the vacuum gas oil in the refineries, and being treated in a FCC unit.

**CONDITIONS**

**Materials**

***PE:*** LDPE, supplied by Dow Chemicals
***VGO:*** Vacuum Gas oil, supplied by Repsol
***FCC equilibrium catalyst:*** supplied by Repsol

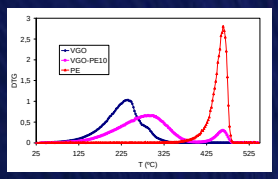
**Experimental conditions**

***VGO-PE blend:*** Jankel & Kunkel IKAVISC MR-F12 mixer by continuously stirring for 120 min, at 60 rpm and at temperatures of 120ºC.
***TGA:*** Netzsch TG 209 thermobalance, ratio catalyst:sample 7:1, 30-550 ºC at 5 ºC/min, nitrogen flowed at 45 STP ml/min.
**Reactor:** 30-550 ºC at 5 ºC/min, nitrogen flowed at 150 STP ml/min.
***GC-MS:*** Agilent GC 6890N, with a GS-GasPro column (30 m x 0.32 mm I.D.)

## Study of the pyrolysis by TGA

To program the temperatures for collecting the samples in the vertical reactor, thermogravimetric experiments were carried out at the same conditions.

### Thermal Pyrolysis

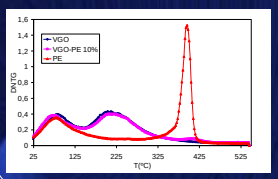



PE shows a single decomposition step
The interval of temperature selected was 350-550ºC.

VGO: the decomposition and/or evaporation occurs in the range of 150-350ºC.
The interval of temperature selected was 100-550ºC.

VGO-PE blend, two decomposition steps appear, the first associated with the decomposition of the VGO, and the second related to the PE decomposition.
The interval of temperatures selected was 100-550ºC.

### Catalytic Pyrolysis




In all the cases the first stage is related to the loss of the water adsorbed over the catalyst.

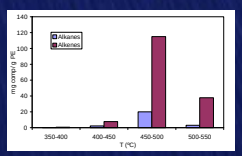
The decomposition of the samples occurs at slightly lower temperature than the value observed in the absence of catalyst, so some catalytic effect of the equilibrium FCC catalyst occurs.

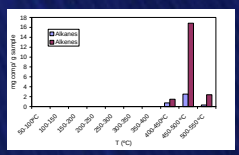
The interval of temperatures selected for collecting the product samples was 50-500ºC for VGO and VGO-PE blend, and 300-500ºC for the case of PE.

## Study of the effect of the temperature: Thermal pyrolysis

**VGO:** The thermal pyrolysis of VGO do not yield gaseous product, but occurs a process similar to a fractionated distillation.

| PE | VGO-PE Blend |
|---|---|
| • Gaseous fraction and a liquid fraction was collected.<br>• The main generation of products has been obtained in the 450-500ºC range.<br>• In all the studied intervals, alkenes are the more abundant compounds.<br>• The major compounds generated are the C4 and the C6<br>• 1-hexene the major compound generated in the main interval of degradation. | • Only appear gases in the interval associate with the PE decomposition<br>• As in the case of PE, the main generation is in the 450-500ºC interval, being n-alkenes the more abundant compounds.<br>• These results indicate that PE and VGO evolve in practically independent steps. |

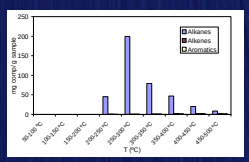



## Study of the effect of the temperature: Catalytic pyrolysis

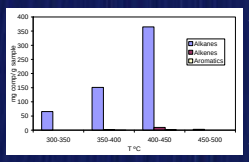
1. The catalyst interacts in some way with the three samples, including VGO.
2. The yield of gases increases with respected to the thermal process.
3. The selectivity of products changes to the formation of alkanes
4. The main alkanes generated were iso-alkanes

**VGO**



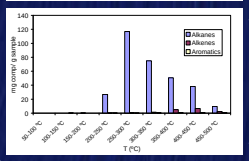

• Gases were generated.
• The main interval of decomposition is 250-300 ºC.
• In the main interval, the more abundant are C6 alkanes, although the major compound collected is iso-pentane.
• When the temperature increases the selectivity changes towards compounds with lower number of carbon atoms.

**PE**




• The interval of maximum generation of gases is 400-450ºC.
• In all the intervals the formation of C4 alkanes is favored.
• iso-butane is the major compound.

**VGO-PE**




• Two stages of decomposition appear: associated with VGO (alkanes formation) and with PE (alkenes formation).
• In the interval of VGO decomposition: the formation of iso-pentane is favored.
• In the interval of PE decomposition: iso-butane is the major compound.

## CONCLUSIONS

- In the thermal pyrolysis process, VGO was not degraded, and only a fractionated distillation occurs.
- I n the thermal decomposition of the PE n-alkenes were favoured, and 1-hexene is the main compound.
- In the thermal decomposition of the VGO-PE blend, gases were only collected in the interval of decomposition associated with the degradation of the PE, being n-alkenes the major group of compounds.
- In the catalytic decomposition of VGO, PE, and VGO-PE blend, the compounds favoured are the iso-alkanes.
- The catalytic decomposition of the VGO yields gases, and the major compound observed is iso-pentane.
- The catalytic pyrolysis of the PE reflects that iso-butane is the more abundant compound.
- The behaviour of the VGO-PE blend suggests that the two processes involved in the catalytic pyrolysis process occur mainly in independent ways, and in the interval of temperature associated with the decomposition of the VGO the major compound is iso-pentane, whereas in the interval associated with the decomposition of PE, is iso-butane.
- As a conclusion, the results obtained in this work indicate the ability of the treatment of the VGO-PE blends in a conventional FCC process as an alternative way for plastic recycling, because the presence of the polyethylene does not affect considerably the composition of the gases with respect to the VGO, adding an additional decomposition step at higher temperatures. Moreover, its presence favours the formation of iso-butane, propane, and butane, which forms part of the liquefied petroleum gas (LP).

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