

Comparative Study of Different Atmospheres for a PtPd/Y Catalyst Regeneration for Plastics/VGO Hydrocracking

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The valorisation of post-consumer plastics by co-feeding them to hydrocracking units has been gaining attention due to their feasibility to produce automotive-like fuels with a composition suitable for commercial use. For this purpose, the use of noble metal-based catalysts is advised due to their high selectivity towards these fractions and high hydrocracking activity. In this context, the reuse of such catalysts should be explored to avoid expensive operating costs. This work explores different regeneration atmospheres of a PtPd/Y zeolite catalyst used in the hydrocracking of polystyrene (PS)/vacuum gasoil (VGO) blends (10 wt%) under the following conditions: 400 °C, 80 bar, 180 min, catalyst/feed ratio: 10 wt%. Regeneration has been carried out under oxidizing, reducing and gasifying conditions using oxygen, hydrogen and CO₂ as regenerating agents. The results reveal that only controlled combustion provides efficient catalyst regeneration, yielding almost the same yield distribution and chemical composition of the liquids, with less than a 5 wt% difference in both cases. The activity decay is attributed to irreversible causes of deactivation that are minimal in the actual process, thus encouraging the adoption of this valorisation pathway for the exploitation of crude resources in terms of maximizing refinery conversion while promoting the Waste Refinery.

1. Introduction

In recent years it has been pointed out that the world is facing a critical situation in terms of energy availability. Historical issues such as the geographical availability of resources as well as situational issues such as geopolitical conflicts or environmental awareness are redirecting the energy scenario. In this context, crude oil has been a key commodity in recent decades, with a wide variety of applications following its processing. Among these applications, polymer production has carved a niche for itself in the petrochemical industry due to the exceptional properties of these materials and their application in a wide variety of fields such as agriculture, construction, medicine and industry.

The increment in the demand for plastics has led to a huge increase in their production, which reached 368 · 10⁶ tonnes in 2019, excluding PET, PA and polyacrylic fibres, and representing a 2.4% increase over the previous year (Plastic Europe, 2021). Until now, after the life cycle of plastics, most of them were discarded in landfills or taken to incinerators to recover part of the energy contained in them through direct combustion. The problems of waste accumulation and emissions from uncontrolled combustion (many of which are considered potentially hazardous) have curbed these practices as far as possible (Tong et al., 2023). While attempts at a more sustainable lifecycle have focused on the more advanced countries, mainly through the introduction of recycled plastics into the production chain, some developing countries cannot keep up with the pace of developments they are experiencing whilst imposing the same level of restrictive measures in the environmental area. As a result, the exploitation of oil resources is set to remain intensive in the years to come, slowing down the decarbonisation targets set out in some agreements. In addition, some of the measures do not stop the production of virgin plastics, so that the volume of plastic waste at the end of its useful life will continue growing. Plastic waste can be a great source of contained energy that has traditionally been overlooked. The composition of different polymers (due to the heterogeneity of their elemental composition but also due to the introduction of additives) negatively influences the ecosystem and human health whether accumulated or incinerated.

However, the base composition of these materials is based on large amounts of carbon and hydrogen, so that there is a high interest in their proper handling after their useful life is over (Ismail and Dincer, 2023). While the reuse of plastics is a palliative to waste generation, the increasing presence of polymers with a heterogeneous nature in municipal solid waste (MSW) makes it necessary to look for alternative ways to deal with such waste. To this end, some of the usual refinery operations are being optimised and studied as viable methods for the absorption of waste and new materials, giving rise to what is known as the Waste Refinery.

Waste Refinery includes those processes aimed at the large-scale implementation of the reconversion of waste from the consumer society (plastics, tyres) and the transformation of other resources such as biomass to limit the negative effects of conventional methods on the environment (Palos et al., 2021). Among others, pyrolysis, gasification and hydroprocessing have been positively recognised as alternatives to deal with plastic wastes in particular. If the focus is on the latter, hydroprocessing of plastics is gaining attention for the combination of simultaneous polymer degradation with heteroatom reduction and quality adjustment of the resulting streams (Narksri et al., 2022). For the same reason, their co-feeding with regular refinery streams is being studied lately with results that encourage the implementation of this valorisation route on a large scale.

Among the variants of hydroprocessing, hydrocracking employs medium-severe operating conditions in terms of temperature and hydrogen pressure to achieve hydrogenation, hydrogenolysis and cracking reactions. To this end, the use of bifunctional catalysts has been one of the main objects of study, since they provide a promotion in the aforementioned functions (Vedachalam et al., 2021). However, noble metals have levels of activity and selectivity towards the streams of interest that stand out and put the focus on the minimisation of deactivation factors for their use in continuous operations.

For the development of industrial catalysts, activity, selectivity and stability are the cornerstones. The deactivation of bifunctional catalysts using zeolites as support is caused by coke deposition, metal poisoning, sintering of the active phase and attrition (Ancheyta et al., 2005). Although the last two can be minimised by correctly adjusting the operating conditions, the first two are inherent phenomena in refinery processes and are therefore the main causes of catalyst deactivation in hydrocracking. In order to study the restoration of catalyst activity, the nature of the deactivation phenomena affecting the catalyst must be considered. Thus, while the deposition of coke has usually been solved in industry by burning it off using high temperature air currents, the deposition of metals affecting catalytic activity is a permanent phenomenon. In addition, the combustion of coke deposits can modify the properties of the catalyst due to the formation of hot spots or high local temperature gradients due to the exothermic nature of these reactions. For these reasons, the use of regeneration conditions and regeneration agents must be carefully studied and selected so that the subsequent reactions reproduce the original process in the best possible way (Zhou et al., 2020).

In this work, the regeneration of a platinum and palladium catalyst supported on zeolite Y in different atmospheres has been studied by maintaining the reaction temperature in order to avoid thermal modifications on the support. For this purpose, three different agents have been used: combustion with an oxygen stream diluted in nitrogen, gasification with CO₂, and hydrogenation with a hydrogen stream. The reactions with fresh and regenerated catalysts were carried out at 400 °C, 80 bar, 180 min and with plastic/feed and catalyst/feed ratios of 10 wt%. The regeneration atmospheres were composed of the following gas mixtures: 5 vol% O₂-95 vol% N₂, 37.5 vol% CO₂-62.5 vol% N₂ and 37.5 vol% H₂-62.5 vol% N₂.

2. Experimental

2.1. Feeds

The vacuum gasoil (VGO) used in the reactions comes from the vacuum distillation tower of the Petronor refinery (Muskiz, Spain), and its properties are listed in Table 1. The density was determined with a digital density meter following the procedure established in the ASTM D4052 Standard. The average molecular weight as well as the chemical composition by groups (saturated and aromatic) were estimated by SAR analysis with an HPLC, while the asphaltene content was determined following the ASTM D3279 Standard. For the determination of the simulated distillation curve, an Agilent Technologies 6890 gas chromatograph equipped with a DB-2887 semi-capillary column and a FID detector was used, according to ASTM D2887. Finally, the elemental analysis was performed on a LECO TruSpec CHN Macrom.

The polystyrene (PS) was purchased from Dow Chemical (Tarragona, Spain) in the form of 4 mm cylindrical pellets, which were ground before being introduced into the reactor by means of a cryogenic mill using liquid nitrogen. The most remarkable properties of PS are a density of 1.030 g mL⁻¹, a molecular weight of 311.6 kg mol⁻¹ and a dispersity of 2.39.

Table 1: Properties and elemental composition of the VGO

Properties	
density at 15 °C (g mL ⁻¹)	0.92
average molecular weight (g mol ⁻¹)	413
IBP–FBP (°C)	408–503
Asphaltenes (wt%)	0.1

2.2. Catalyst

A bifunctional PtPd/Y catalyst synthesised in-house has been used for this work. The Y zeolite (CBV-712) was acquired from Zeolyst International, while the metal precursors (platinum and palladium nitrates) were purchased from Sigma-Adrich. The synthesis procedure consists first of calcining the zeolite at 550 °C for 15 h to give it thermal stability. Afterwards, the impregnation of the metals was carried out at 80 °C, maintaining a neutral pH for 24 h. After this time, the solution was dried in a rotary evaporator at vacuum and 80 °C and left to dry overnight at 110 °C. The resulting solid was calcined at 450 °C for 4 h and the resulting catalyst was sieved to a particle size between 150-300 µm.

Catalyst properties are listed in Table 2. Textural and surface properties were determined in a Micromeritics ASAP 2010 equipment by nitrogen adsorption-desorption isotherms at -196 °C and prior samples degasification at 150 °C for 8 h. Surface was determined according to BET procedure, whereas micropore volume was determined with t-plot method and average pore size was estimated applying the BJH model. Total acidity was determined through ammonia temperature programmed desorption in a Micromeritics AutoChem II 2920 apparatus. Metal content quantification was obtained from a Thermo X7-11 quadrupolar mass spectrometer, provided with an Xt interphase and a concentric nebulizer for performing inductively coupled plasma emission spectroscopy (ICP-AES). Concerning the metal dispersion, it was measured in through CO chemisorption in a Micromeritics AutoChem II 2920 equipment coupled in line with a Blazer Instruments mass spectrometer. The sample was previously reduced at 300 °C with hydrogen (10 vol%) in Ar for 1 h and then stabilized at 60 °C. Then, pulses of 0.25 mL were emitted until the sample is saturated. For the calculation of metal dispersion, the stoichiometric coefficients of both metals were established at the unity.

Table 2: Properties of the fresh PtPd/Y catalyst

Textural properties	
S _{BET} , m ² g _{cat} ⁻¹	548
S _{micropores} , m ² g _{cat} ⁻¹	368
V _{micropores} , cm ³ g _{cat} ⁻¹	0.163
D _{pore} , nm	7.9
Acidic properties	
Total acidity, mmol NH ₃ g ⁻¹	0.465
Metallic properties	
Pt content (wt%)	0.44
Pd content (wt%)	0.5
Dispersion (%)	47.8

2.3. Reaction and regeneration equipment

Prior to the reaction, the catalysts were reduced ex situ in a fixed bed reactor at 400 °C for 4 h in a hydrogen stream diluted in nitrogen (37.5:62.5 v/v) to ensure the active form of the metals was obtained. The regeneration of the catalyst was also carried out in the fixed bed reactor at 400 °C and atmospheric pressure using the following flows (total flowrate of all streams, 100 mL min⁻¹): 5 vol% O₂-95 vol% N₂, 37.5 vol% CO₂-62.5 vol% N₂ and 37.5 vol% H₂-62.5 vol% N₂. The regeneration time was tested under the different atmospheres at increasing times with an interval of 3 h up to a maximum time of 15 h, which corresponds to the complete combustion time of the coke under the oxidizing atmosphere. However, only the longest time is compared because of the little effect of the low times under the other regenerating agents. The hydrocracking reactions were carried out in a 50 mL stirred tank reactor (MicroClave, Autoclave Engineers). The operating conditions used are as follows: temperature, 400 °C; pressure, 80 bar; reaction time, 180 min; catalyst to feed ratio, 0.1. The system operates in a semi-continuous regime, with an initial total load of 20 g and a continuous flow of 100 mL min⁻¹ of hydrogen. The reaction gases yields were quantified by weight difference between the system before and after the reaction and analysed cryogenically (-30 °C) in a gas chromatograph (Agilent GC 6890). The coke formed during the reactions was estimated by thermogravimetric analysis - temperature programmed oxidation (TG-TPO) on a thermobalance (TA Instruments TGA-Q 5000). Finally, the yield of the liquid product was calculated by difference

between the feed and the other phases, its composition was determined by two-dimensional chromatography on an Agilent 7890A GC × GC - MS and the simulated distillation curve was obtained on a gas chromatograph (Agilent GC 6890) according to ASTM D-2887.

The distinction between the different product fractions was made according to the boiling point criterion: dry gas (DG), liquefied petroleum gases (LPG), naphtha (< 216 °C), diesel (216 < TBP < 343 °C) and gasoil (heavy cycle oil, HCO, TBP > 343 °C). To assess the extent of the reactions, the yield of each of the lumps considered has been defined according to Eq(1). In addition, coke, as it is produced from the feed mass, has also been considered as a product fraction. The composition has been analysed according to the different chemical families: n- and iso-paraffins (nP, iP); naphthenes (N); olefins (O); and mono-, di- and poly-aromatics (A₁, A₂ and A₃₊, respectively).

$$Y_i = \frac{m_i}{m_{\text{total}}} 100 \quad (1)$$

3. Results

The yield distribution of the PS/VGO hydrocracking products, utilizing both fresh catalyst and those that have been regenerated using the methodologies explained above, is shown in Figure 1. From comparing the results of regenerated catalysts to those obtained using a fresh catalyst, it is clear that only carefully regulated oxidation of the spent catalysts can produce a regenerated catalyst with an activity that is comparable under the investigated conditions. After oxygen controlled combustion of the deactivated catalyst, the yield of the lumps of interest (i.e. naphtha and LCO) hardly decreases, showing a difference of less than 0.5 wt% with respect to those yields obtained with the fresh catalyst. The main difference between the fresh catalyst products and the combustion-regenerated catalyst products is found in a higher HCO yield corresponding to a lower LPG mass yield, this difference being 2 wt.%. It should be noted that hydrodemetallisation reactions (associated with irreversible deactivation by metal deposition) can take place at the micropore openings and that the accumulation of metals removed from the bulk molecules accumulate to form aggregates (Ramirez-Corredores, 2017).

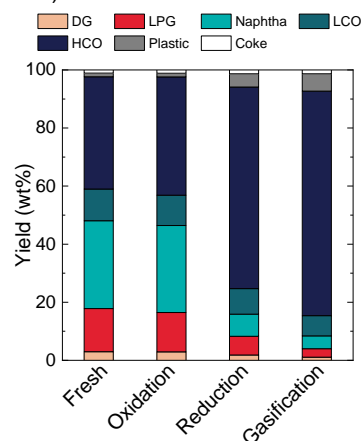


Figure 1: Yields distribution for fresh and regenerated catalysts

The observed decrease in activity may be because this mechanism does not exclusively affect the hydrogenation function (which is usually more affected) but also physically influences the support cracking function through this blockade. Using hydrogen to remove deactivating molecules or carbon dioxide to encourage their oxidation is not practicable, since the conversion of the HCO fraction is limited in these cases. PS is not converted, demonstrating that low activity levels lead to the degraded polymer fouling over the catalyst and provoke the total catalyst activity inhibition, similar to what was observed in previous studies at 380 °C. The development of coke species in the same environment and at greater partial pressures renders hydrogen unable as an agent for converting those compounds. On the other side, the regeneration potentials offered by CO₂, which have been demonstrated to be effective at higher temperatures due to the extremely endothermic nature of coke gasification, show no good results in this process. Moreover, a rise in temperature can compromise the support's thermal stability, thus it might be advised to conduct further research on this possibility and include CO₂ valorisation in the entire procedure.

The extent of the different regenerations is also reflected in the composition of the liquid fractions of interest, i.e. naphtha and LCO, the distribution of which is shown in Figure 2. Following the classical mechanisms of catalytic deactivation in hydrocracking, the effect is most pronounced in the loss of aromatics conversion capacity of the

catalyst. The deposition of coke and the possible lack of its complete removal reduce not only the scope of cracking reactions but also the hydrogenation capacity of aromatics, which can suffer from addition reactions, dehydrogenation and hydrogen transfer under these conditions (Vivas-Báez et al., 2021). Thus, in cases where the catalyst has not been effectively regenerated, a higher concentration of aromatic compounds is obtained with respect to the concentration obtained in the fresh catalyst products at the expense of decreasing the isoparaffin content, resulting from the ring-opening mechanism in the hydrocracking reactions. In the case of regenerating in a controlled oxidizing atmosphere, the effect of this catalytic decay is smaller, producing variations in general less than 5 wt% in both naphtha and LCO. The deposition of strongly chemically adsorbed metals affects the catalytic activity both by competitive adsorption with the reagents and by modification of some properties such as geometry or structure. (Rodríguez et al., 2018). These metals (such as Fe and Ni), often present in crude derived streams, affect the HDA function of catalysts in hydrocracking. The most prominent change is that observed in the concentration of monoaromatics in naphtha (with an increase of 5.6 wt% when using the oxygen-regenerated catalyst), although its production can be attributed exclusively to the refractory character of the 1-ring aromatics. The yield of the plastic obtained with the oxygen regenerated catalyst is very similar to that obtained with the fresh catalyst, so it cannot be assumed that the monoaromatics seen in naphtha come from a lower conversion of this reagent.

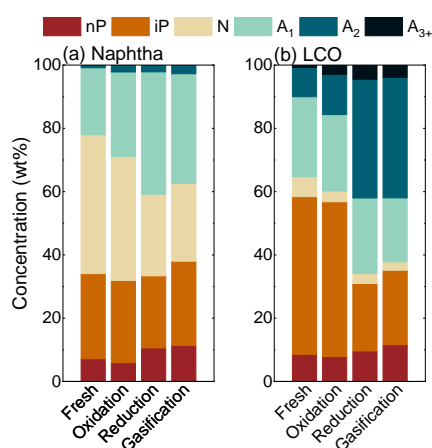


Figure 2: Composition distribution for fresh and regenerated catalysts of a) naphtha and b) LCO fractions

To understand the effect of deactivation and the different regeneration atmospheres tested on the catalyst, the textural properties of each were measured and are shown in Figure 3. First, reduction and gasification confirm the lack of regeneration by presenting external surface area values well below the value of the fresh catalyst. In fact, the deposition of coke (formed by polyaromatic compounds) is known to block the micropore channels, which corresponds to the drastic drop observed in the volume of such pores. As for the oxidatively regenerated catalyst, a reduction in both surface area (497 $\text{m}^2 \text{g}^{-1}$) and pore volume (0.174 and 0.142 $\text{cm}^3 \text{g}^{-1}$ of micro- and mesopores volume, respectively) is also observed, attributable in this case to the formation of aggregates formed by the accumulation of deposited metals from the VGO. These formations can be located both near the metals of the catalyst, hindering the hydrogenation function, and at the mouths of the pore systems, hindering the access of the molecules to the active centres.

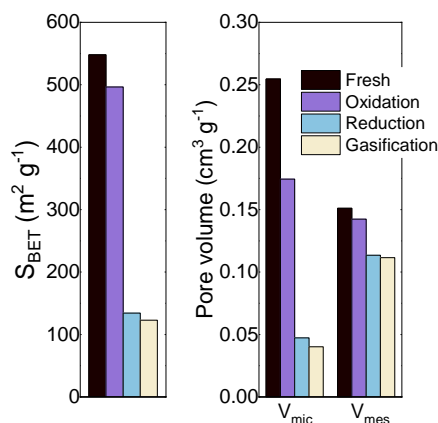


Figure 3: Textural properties of fresh and regenerated catalysts

4. Conclusions

The hydrocracking of PS and VGO has shown to be a viable alternative for the treatment of plastic wastes obtaining remarkable yields to fractions of commercial interest as fuels with a suitable composition. The results of this work propose that the only viable option for the regeneration of the catalyst in order to use it in continuous operation is the controlled oxidation of the coke deposits. Through this regeneration process it is possible to recover almost all the catalytic activity, keeping the final yield of the plastic to a minimum and with only a 5 wt% increase in the aromatic content of the naphtha and the LCO. The margin of loss can be attributed to irreversible deactivation by metal deposition on the catalyst, which has an absorption limit and after which the catalyst activity could be assumed stationary, while the properties of the catalyst are minimally affected by the limited severity of the regeneration process. This contributes to the intensification of the process not only in terms of feeding waste but also by reducing the amount of fresh catalyst used and deactivated catalyst disposed of as waste.

Nomenclature

Y_i – yield of each i lump, wt%
 m_i – mass of each i lump, g
 m_{total} – mass of total products, g
 S_{BET} – surface area, m^2

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