

Increased Profitability in the Production of Propylene and Derivatives in a Refinery

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ABSTRACT

The global challenge of decarbonization of society forces all economic activities to a thorough review of their processes. The Galp group intends to transform its Sines refinery into a green energy hub by 2030, by implementing energy efficiency initiatives and projects to reduce its carbon footprint.

Currently, in the FCC unit of its refinery at Sines, propylene is a by-product that presents a great potential for valorization and a growing projection of demand, with annual growth rates of 6% globally. Combined with the need to reduce the production of polluting fuels, this growth represents an opportunity for the company.

The challenge proposed in this work is based on evaluating the possibility of increasing propylene yield in the FCC unit, through small changes in its production process, such as increasing the reaction temperature and adjusting the catalyst, namely in the incorporation of additive. On the other hand, it is intended to increase the valorization of this propylene, through an investment in a splitter, which allows obtaining a product of high purity (propylene polymer-grade).

Throughout the project, the contextualization of the problem will be presented, followed by a literature review. Different technologies and possible changes to be applied in the FCC to achieve the proposed objectives will be analyzed. According to several future price scenarios, an economic evaluation will be performed in order to verify that the necessary investments will pay off in the future and this is the right way to go.

Keywords: Decarbonization; Galp; FCC unit; Propylene; Polymer-grade

1. INTRODUCTION

The global challenge of decarbonizing society forces all economic activities, and in particular the energy sector, to a complete redesign of their processes. Due to the predictable reduction in fossil fuel consumption, to ensure the viability of refineries it is necessary to increase the yield in chemicals. This is where the concept of crude-to-chemicals refineries arises, where chemicals are the majority of production, with liquid fuels as the byproduct. It makes sense for refineries to start divesting gasoline production and start investing in the production of chemicals that show growth in the coming years, such as propylene, butylene and ethylene, products that belong to the petrochemical industry. The petrochemical industry is responsible for transforming natural gas and oil derivatives into raw materials with higher added value, which are used in the manufacture of products of great relevance to society. This sector has become

increasingly strategic and important for the economy. The integration of refineries with chemicals is becoming an important growth strategy for many companies. Increasing pressure on refineries due to the energy transition and strong demand growth in both the olefin and aromatics markets, supported by continued global demand for plastic products and synthetic fibers, are key factors in the integration effort.

Currently, in Portugal, Galp's refining complex already has some integration with the petrochemical sector. However, there is still room to maximize the production of chemicals to the detriment of the production of fossil fuels.

The main objective of this paper is to analyze the best technologies and processes available to enable the Sines refinery to maximize the production of propylene in its FCC unit, and the subsequent production of polymer-grade propylene – propylene

with a high degree of purity - in order to create value for the company.

2. PROBLEM DEFINITION

2.1 Galp Energia Group

Galp's history covers three centuries and is largely associated with the industrial evolution in Portugal. Galp has become not only the single leading refiner and distributor of petroleum products in Portugal, but also the largest importer and distributor of natural gas at national scale. Galp positions itself as an integrated energy company that develops profitable and sustainable businesses, aiming to create value for its stakeholders (Galp, 2020b). For over half a century, this organization owned an integrated refining system consisting of two refineries in Portugal, located in Matosinhos and Sines, with a crude processing capacity of around 330,000 barrels per day. In March 2021, as part of its updated strategy, the company concentrated all its refining operations in the Sines plant, discontinuing the Matosinhos refinery.

2.2 Sines Refinery – FCC Unit

The Sines refinery is an asset of Petrogal, SA, a Galp Energia Group company, and began its operations in 1978, having undergone several evolutions over the years. It is one of the largest in Europe, and the main (and now only) refinery in Portugal, with a current distillation capacity of about 10 million tons of crude per year.

Propylene is a by-product of the FCC unit at the Sines refinery and has great potential for recovery. For this reason, this study focuses on this particular unit.

The FCC unit feed charge can be very variable, depending on the refinery's configuration and processing objectives. The quality of the load has a very significant impact on the operation of the FCC units. Currently, this unit's charge is vacuum gas oil (VGO) produced in the refinery's vacuum units I and II, imported VGO, atmospheric residue (RAT), and naphtha from the visbreaker. The charge is transformed through a catalytic cracking process into fuel gas, liquefied petroleum gas (LPG), gasoline, swing-cut, light cycle oil (LCO) and slurry (fuel oil component). After being treated, LPG is separated into propylene, used in the petrochemical industry, and butylene, used as a charge in the alkylation unit. In the FCC unit there is also the

generation of coke on the surface of the catalyst, which is continuously regenerated and returned to the reactor (Agência Portuguesa do Ambiente, 2008).

Galp intends to transform its Sines refinery into a green energy hub by 2030, improving its energy efficiency and reducing its carbon footprint.

2.3 Opportunities & Motivation

The growth of the petrochemical market and the increased demand for propylene require refineries to redefine themselves and look for new business opportunities. Currently, the FCC unit at the Sines refinery obtains about 6.5% yield by weight of propylene. To remain competitive and follow market developments, it is crucial for Galp to study and analyze mechanisms to maximize this propylene production, in order to sell a product that allows for greater profit. The major challenge and fundamental question of this study will be to choose the most cost-effective solution with regard to propylene production that takes into account the expected fuel demand and the highest achievable propylene yield.

3. LITERATURE REVIEW

3.1 Types of Crudes

The type and quality of refined products produced in a refinery depend on the types of crude used as feedstock and the structures installed in the refinery. Crudes can be grouped into sweet crudes - lighter and with a sulfur content of less than 1% by weight in RAT, more expensive - and sour crudes - heavier, with a sulfur content of more than 1% by weight in RAT and cheaper. In 2015, 62% of sweet crude and 38% of sour crude were processed at the Sines refinery (Galp, 2015b). Since January 2020, with the introduction of "IMO 2020" (International Maritime Organization), which required an 80% reduction in sulfur emissions to produce a fuel with a maximum sulfur content of 0.5%wt, the Sines refinery started processing 100% sweet crude.

Galp manages crude oil supplies considering various commercial, technical and environmental requirements and factors such as quality, market availability, international prices, storage capacity, maximization of the refining margin, supply diversification strategy and specificities of the refining system.

The current distillation capacity of the Sines refinery is approximately 226 thousand barrels per day (Galp, 2021a).

3.2 Stages of Refining

Crude oil is composed of several types of hydrocarbons. Refining petroleum is a process that takes advantage of the different weights, volatilities and boiling temperatures of these hydrocarbons in order to separate them into intermediate and final products. There are four main refining stages for separating crude oil into usable substances: physical separation of hydrocarbon types through distillation, purification of intermediates in pretreatment units, chemical processing of lower-value fractions into lighter and more valuable products, and treatment of intermediates by removing undesirable elements and compounds (contaminants) for integration into final products. (Galp, 2020d). Each step in the refining process is intended to create and maximize added value to the raw materials that are processed in it (Galp, 2020a).

3.3 Propylene

Propylene is the second largest volume chemical produced globally and is an important raw material for the production of chemicals such as polypropylene (PP). About 30% of propylene is produced as a byproduct of oil refining, of which 97% is obtained by FCC units (Intratec, 2013).

The global propylene market is expected to grow at a CAGR (compound annual growth rate) of around 6% between 2016 and 2025, due to increasing industrialization (TechSci, 2017).

3.4 Maximizing Propylene in the FCC

The average base yield of propylene in an FCC unit is about 5% by weight of its feed. With strong market demand and the potential ability to achieve higher propylene yields, there is a natural desire to maximize these yields. However, there are competing economic forces suggesting that the optimal propylene yield is 10 to 11% by weight, which is substantially less than current technology can produce (Couch, Glavin, Wegerer, & Qafisheh, 2007).

The increase in propylene yield in the FCC above the base case can be grouped into three ranges (Knight & Mehlberg, 2011):

1. 3% to 5% - through modifications to the catalyst system and an increase in reactor temperature;
2. Between 5% and 9% - The same as in point 1 along with a reduction in the partial pressure of the hydrocarbons. Implementation may require modifications to allow for additional capacity;
3. Greater than 9% - Same as in point 2 along with targeted recirculation of LPG and naphtha. Implementation require reconfiguration of the gas concentration unit to facilitate the use of recirculation. The application of new technology may be considered which will require extensive modifications to the reactor/regenerator section as a second reactor will be added.

Catalytic System

In an FCC unit a catalytic system is used consisting of a mixture of catalyst and additives.

The current catalyst used in the Sines FCC unit is supplied by BASF and is dedicated to naphtha maximization. There are catalysts on the market whose objective is the maximization of propylene, so the replacement of the catalyst is a viable hypothesis to increase the production of propylene in the refinery and to meet the company's expectations.

Additive

Additives are substances that act in a complementary way to the catalyst and have a specific and predefined purpose.

The use of the zeolite ZSM-5 (Zeolite Socony Mobil-5) as an additive for catalysts is well known by experts. ZSM-5-based additives convert olefins from the gasoline range into light (LPG) olefins, such as propylene, while increasing the octane rating of gasoline.

Currently, the Sines FCC unit uses a reduced percentage of an additive called ZIP, which has 40% ZSM-5 zeolite in its composition. The incorporation of ZIP for propylene maximization varies between 10% and 15%, and up to 12% incorporation, the increase in propylene yield is linear: for each 1% of additive, propylene production increases between 0.2% and 0.3%. BASF, supplier of this additive, believes that it is possible to reach 15% ZIP and obtain a yield of

about 10% in propylene. Several additive blends for the purpose of maximizing propylene production are present on the market from different suppliers, as BASF, GRACE and Johnson Matthey. The effects of maximization will also depend on the feedstock, the operating conditions of the unit, and the type of catalyst added to the FCC.

Temperature

Increasing the reaction temperature directly increases the production of fuel gas, propylene and gasoline. Temperature variation is a simple solution that can be implemented immediately, is reliable, and requires no investment on the part of the company.

Technology

The ZSM-5 additive is only capable of cracking C7 to C10 olefins to LPG. Consequently, most of the C5 and C6 cut is not converted by ZSM-5 in the main riser. The optimal catalytic system, in order to overcome this situation, is a recirculation system in a separate riser, which operates under more severe conditions. Axens, a group that provides a range of solutions for converting oil into cleaner fuels, commercializes this technology, and it is patented under the name PetroRiser™ (Axens, 2020). UOP, licensor of Galp's FCC unit, as a technology development company for oil refining, also develops identical technologies.

3.5 Polymer-grade Propylene

The three commercial grades of propylene are:

- Polymer-grade (PG) with a minimum purity of 99.5%;
- Chemical-grade (CG) with a minimum purity of 93%;
- Refinery-grade (RG) with a purity of about 70%.

The Sines Refinery produces a propylene refinery-grade, with a purity of about 75%. The price at which the polymer-grade propylene is sold is about 25% higher than the refinery-grade price. This result provides opportunities for refiners to consider investments that can achieve attractive rates of return. Any. As for polymer-grade propylene recovery, Galp does not yet have any unit capable of performing this conversion, so it will have to

invest in a completely new system to be able to sell polymer-grade propylene and achieve higher profits.

C3 Splitter

The solution for recovering polymer-grade propylene is to install a splitter that separates the propylene from the propane and other light components present in the stream. UOP, Axens, TechnipFMC, KLM are some examples of companies that sell this technology.

4 BASE SCENARIO

The FCC unit at the Sines refinery currently achieves a 6.5% yield by weight in propylene. Operating conditions, the catalyst system and reformulations and upgrades in technology can increase propylene yields by up to a further 5%. Currently only a small % of ZIP is being added and the unit is at about 535°C. To maximize propylene, it will then be necessary to increase the amount of ZIP to 15% and the reaction temperature to 545°C in order to obtain as much propylene as possible, which according to Petro-Sim™ predictions will be 9% by weight propylene.

The propylene obtained in the FCC is considered refinery-grade, and to transform it into polymer-grade (25% more valued than refinery-grade) will require investment because the refinery does not yet have any equipment that allows propylene to be obtained with this purity. There are already new technologies on the market that, based on reformulations and applications of new units, allow the propylene to be purified and sold at a higher price, as opposed to what is done now.

5 FCC UNIT SIMULATION

For the study of the FCC unit, the process simulator Petro-SIM™, from KBC Advanced Technologies, was used.

In order to evaluate the impact of the introduction of new units, changes in yields or raw materials, Galp has a mathematical model of linear programming (PL), which predicts optimized margins.

Thus, the yield forecasts obtained by Petro-SIM™ will be used to feed Galp's linear programming model, and it will be possible to obtain margin estimates for different future price scenarios.

4.1 Price Scenarios

In this study, four possible future price scenarios were used in the Linear Programming model, defined according to the evolution of technology and political consensus, in order to assess the resilience of the project:

- A. Scenario A - demand for electric vehicles increases, diesel maintains tax benefits;
- B. Scenario B – electric vehicles will be the main mode of transport, taxes on diesel will be increased;
- C. Scenario C – efficiency gains are low and electric vehicle penetration will also be low, with no change in fuel taxes;
- D. Scenario D - diesel will have higher taxes, the renewable energy directive targets will be revised, boosting biofuels.

The long-term Brent price outlook for each of the scenarios will be different, depending on market behavior. It only makes sense to invest in maximizing propylene when it is more highly valued than gasoline (Table 1).

Table 1 - Δ Propylene and Gasoline prices per scenario (\$/t)

Scenarios	A	B	C	D
Year	2025			
Δ C3 vs GA \$/t	112	233	-42	44
Year	2030			
Δ C3 vs GA \$/t	116	225	-25	41

The analysis of yields will only be done under conditions of scenario A and B, as these are the scenarios with promising futures for propylene exploration.

4.2 Refining Margins

Using the PL model, the propylene margins for scenarios A and B for 2025 and 2030 were obtained, in M\$ per year (Table 2).

Table 2 - Propylene Refining Margins in M\$/y, from PL (M\$/y)

Scenarios	A	B	A	B
Year	2025		2030	
Δ Maxi-Propylene (M\$/y)	8.18	19.46	6.13	21.49

Converting to euros, the delta of the annual margin that is obtained to produce maxi-propylene in scenario A is about 7.03M€ in 2025 and 5.27M€ in 2030. For scenario B, in 2025 the increase in margin will be 16.74M€ per year and in 2030 it will reach 18.48M€.

To study the Maxi-Propylene, the operating conditions had to be changed in the simulation of the FCC unit. It was necessary to remove the limit of some flows that were already operating at their maximum. At least the Fuel Gas flow rate, the LPG flow rate and the gas compressor flow rate exceed their current limits and will therefore need revamping. The temperature has also been increased from 536°C to 545°C, and the amount of ZIP additive added has been changed to 15% (that makes 6% ZSM-5). With these changes, on average, propylene increases its yield by about 3-4%, which is a very positive result that represents almost 82 thousand tons of propylene produced per year that are converted into 81 thousand tons exported for scenario A in 2025, and 86 thousand tons of propylene/year that are converted into 85 thousand tons exported, for scenario B of the same year. In 2030, for scenario A we have a production of almost 84 thousand tons with 83 thousand tons exported and for 2030, 100 thousand tons produced, and 99 thousand tons exported, per year.

6 ECONOMIC EVALUATION

An economic and financial feasibility study is fundamental to evaluate the cost of a possible investment project to be carried out and its impact on the company. One of the most important aspects in determining the overall economic viability of a chemical process is determining the capital cost. In addition to the purchase price of the equipment, capital costs include the delivery and installation of the equipment, the preparation of the land for construction, the salaries of contractors and construction workers, and any other costs associated with the construction of a chemical plant. It is necessary to consider that there are several known bottlenecks, and probably some unknown ones as well, when calculating capex. After consulting the teams responsible for the refinery's operation and also BASF, it was confirmed that there are limitations at various points in the process, such as in the reactor, the main fractionator, the wet gas compressor, the light derivative streams, the LPG merox, the amine unit, and the alkylation unit,

among others. After all these costs have been determined and estimated, it can be concluded that an investment of about 50M€ will be required to enable the refinery to produce and maximize propylene in the FCC unit. This figure has been calculated with an accuracy range between -20% and 35%.

6.1 Payback Time

The payback period is a financial performance indicator that is widely used in companies to analyze the payback period of a project. It will be measured in years, and the formula is:

$$\text{Payback Time} = \frac{\text{Initial Investment}}{\text{Annual Payback}}$$

Two distinct investments were evaluated: one for the maximization of propylene yield in the FCC unit (propylene refinery-grade), and a subsequent investment in the recovery of this propylene through a splitter (propylene polymer-grade).

Maxi-Propylene

For an investment of 50M€, and with the annual gains considered for each scenario, the payback time for scenario A is approximately 9 years and for scenario B 3 years, representing a much more immediate and interesting return when compared to scenario A (for convenience, it was considered that the annual gain will be the minimum value between the 2025 and 2030 Maxi-Propylene margins).

Propylene Polymer-grade

A value of 29M€ was assumed for the investment in a C3 splitter. In this way, and considering that polymer-grade propylene is about 25% more valuable than refinery-grade, the profitability of this additional investment can be estimated. The efficiency of a splitter varies with several factors. For simplicity, it will be considered for the study a splitter with a yield of 85%.

According to the quantities of maxi-propylene produced in each scenario, the margin that could be obtained when producing polymer-grade propylene was estimated (Table 3).

Table 3 - Valuation of propylene margins for each scenario, using the splitter (M€/y)

Scenarios	A		B	
	Year	2025	Year	2030
Δ Refinery-Grade (M€/y)	7.27	16.74	5.27	18.48
Δ Refinery-Grade (M€/y)	7.47	17.78	5.60	19.63

Considering the same assumptions used to calculate the payback time of maxi-propylene, and considering that to the investment of 50M€ would have to be added 29M€ related to the splitter, it's possible to obtain the payback time for both scenarios. For an investment of 79M€, and with the annual gains considered for each scenario, the payback time for scenario A is approximately 14 years and for scenario B approximately 4 years, representing a much more immediate and interesting return when compared to scenario A.

7 CONCLUSIONS & FUTURE WORK

Refineries in mature markets are reviewing their business models and technology options in response to slowing fuel demand and continued strong growth in global petrochemical demand. The most selective strategy to increase the C3 yield in the GALP FCC is to use a combination of reactor temperature and ZSM-5 based additives. In this study, the achievable propylene margins were calculated assuming that the ZIP additive is maintained, but in higher concentrations (15%) and with the reactor temperature at 545°C instead of 536°C. Four possible future price scenarios (propylene and gasoline prices) defined according to the evolution of technology and political consensus were presented, but only scenarios A and B were studied, since they are the ones that value propylene more than gasoline.

Currently, the propylene yield of Galp's FCC is 6.5%wt. The preliminary goal was to obtain a higher propylene yield, with only a few modifications to the unit flow limits. For the scenarios analyzed, it is observed that propylene increases its yield by about 3-4%, which is a very positive and expected result.

After maximizing propylene, it was further studied the possibility of conversion into high purity propylene, using a C3 splitter, in order to make the

refinery capable of producing high quality propylene and thus increase its revenues.

The investment required for propylene maximization in the FCC is 50M€ and the investment considered for the splitter will be 29M€, for a total of 79M€. The payback in scenario B is much more motivating than in scenario A, varying between 3 to 4 years (B) and 9 to 14 years (A), depending on the type of investment made - whether only in maxi-propylene or also contemplating the recovery of polymer-grade propylene.

The economic evaluation showed the potential of this project, forecasting an increment in the propylene gross margin and proving the technical relevance of the study.

As future work, Galp will proceed with a feasibility study, hiring a specialized company that aims to understand in detail the feasibility of the project. This study will provide a complete analysis of possible investments, allowing for a more rigorous assessment and, subsequently, a clearer decision for future implementation.

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