

Co-Processing of Light Gasoil and Used Cooking Oil in a Hydrotreatment Industrial Unit



De Paz Carmona H^{1*}, Brito Alayón A¹ and Macías Hernández JJ²

¹Chemical Engineering Department, University of La Laguna (ULL), Spain

²Refinery Cepsa Tenerife, Spain

*Corresponding author: De Paz Carmona H, Faculty of Chemistry, Chemical Engineering Department, University of La Laguna (ULL), Con. San Frco. De Paula, San Cristóbal de La Laguna, Spain.

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Introduction

The European Union (UE) renewable energy requirements for next years, are working as engine to develop new, more efficient and environmentally friendly bio-fuels. The hydro-treated vegetable oil (HVO) or Green diesel is a paraffinic diesel fuel produced via catalytic hydro-treatment of vegetable oils at high temperature and pressure [1]. The co-processing of triglycerides feedstocks such

used cooking oils (UCO), in an industrial hydrodesulphurization unit could be very attractive for refineries. It is because not only can be employed the existing installations [2], but it is obtained a bio-fuel that is integrated with the desulphurized gasoil, improving some of their properties such as density at 15 °C and flammability. At the industrial conditions (350-370 °C and 70-80bar), the triglycerides are hydrogenated according with the pathways of Figure 1.

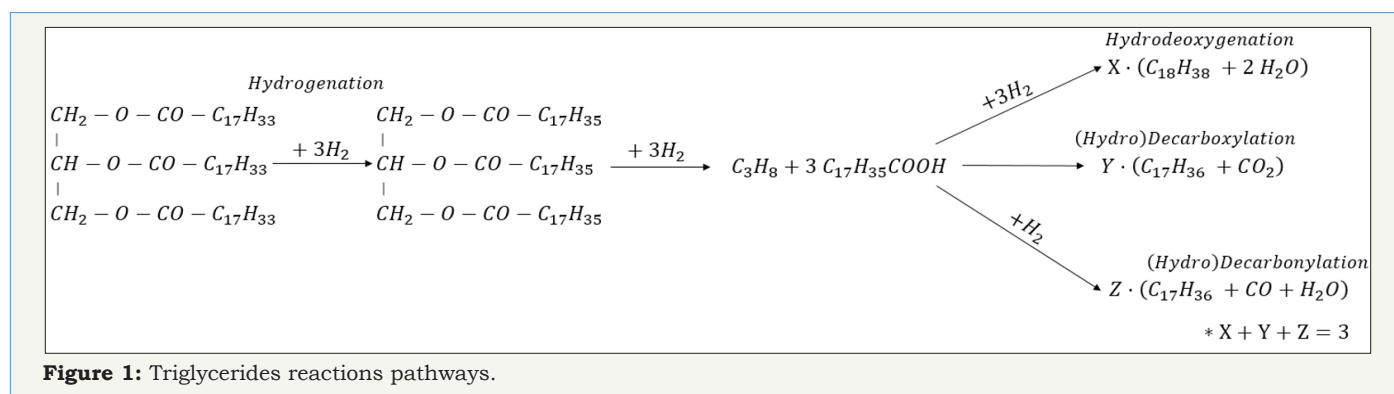


Figure 1: Triglycerides reactions pathways.

Material and Methods

Table 1: Operating conditions used in co-processing experiments.

Parameter\Experiment Nr	1	2
Temperature °C	350	370-380
Pressure, MPa	7.0 - 7.2	7.0-7.2
WHSV, h ⁻¹	0.85	1.30-1.60
H2 to oil, NI/l	220	200
UCO, wt. %	10	5
Feed flowrate, bbl/day	12,000	17,000-21,000
Time of Co-processing, h	24	48
Catalyst	CoMo/Al ₂ O ₃	NiMo/Al ₂ O ₃

Two experiments of co-processing of light gasoil (LG) and UCO were carried out in an industrial unit of hydrodesulphurization HDS-I of Cepsa refinery in Tenerife. Table 1 shows the operating conditions of each experiment. The experimental procedure was divided in two stages: blank run, without vegetable oil, and co-processing. After reached the steady state in each stage, were recollected and analyzed (density at 15 °C, sulphur and nitrogen content, SimDis, composition, etc.) liquid and gaseous samples.

Results and Discussion

The main product obtained from UCO hydro-treating was the HVO (75.3-88.1wt.%), mainly composed by linear paraffins with 15-18 carbon atoms. On the other hand, the by-products produced were water (2.7-15.8wt. %) and light gases (9.1-8.9wt.%) [3]. To determine the pathways promoted by the catalyst, Figure 2 shows the paraffins distribution in the liquid products. The hydrode-

oxygenation reaction was promoted rather than HDC pathway in both experiments, particularly with NiMo/Al₂O₃ sulphured catalyst.

This pathway implies a higher consumption of H₂ as well as water production instead CO or CO₂.

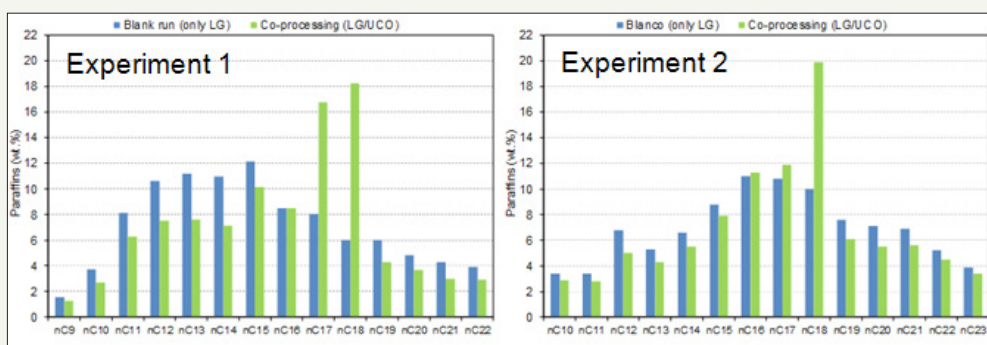


Figure 2: Paraffins distribution. Experiment 1 and 2.

The increment of paraffins produced an alteration of some properties of the desulphurized gasoil. Table 2 shows a comparison between the desulphurized gasoil produced during the blank run and the co-processing. The co-processing of UCO produced a lighter gasoil [3], with a higher value of flammability and cetane index. However, it was observed a little deterioration of some of the cold flow properties as the cloud point. The UCO addition into the feedstock did not produce a significant decrease of the catalyst activity, determined as the capacity of the catalyst to remove the sulphur content from the light gasoil. This behavior probably indicated an adequate number of active site in the catalyst to occur the HDS and de-oxygenations reactions at the same time without mutual inhibition.

Table 2: Desulphurized gasoil properties.

Parameter	Experiment 1	Experiment 2
Density at 15°C, kg/L	–*	–
Cetane index	+	+
Flammability, °C	+	+
Cloud point, °C	+	+
CFPP, °C	=	=

* “+” higher, “–” lower and “=” equal than the values of the desulphurized diesel from blank run.

Conclusion

The main product produced during the UCO co-processing was the HVO (75-88wt.%), composed mainly by linear paraffins with an even number of carbons, which means a promotion of HDO instead HDC pathway. This increment of paraffins produced an improvement of some critical parameter of the desulphurized gasoil as density, cetane index or flammability without a significant interaction with the activity of the catalyst. Thus, the co-processing of UCO is a viable option to obtain bio-fuels at industrial scale using the existing structure of a refinery.

Acknowledgment

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