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Preliminary chemical process for triolein hydrotreatment on a pilot scale using aerogel catalyst based on NiMo carbides

João Pedro Leal Maran[1], João Lourenço Castagnari Williman Pimenta[2], Luiz Mario de Matos Jorge[3].

ABSTRACT

One of the challenges of modern society is to produce renewable and economically competitive fuels, reducing carbon emissions and dependence on fossil sources such as oil. In this scenario, the hydrotreatment of vegetable oils has been studied in a wide variety of catalysts and chemical processes, and is also capable of producing other green fuels such as naphtha, propane and jet fuel. The present work proposes a preliminary chemical process for the hydrotreatment of triacylglycerides using the aerogel catalyst based on nickel and molybdenum carbides supported in alumina, using data reported in previous literature. The simulation of the chemical process was conducted using (PIMENTA, 2020) the Aspen Plus software, version 14, in pilot production scale with triolein as the only liquid-phase reagent fed into the system, considering a hydrogen/triolein ratio of 0.037975 and a trioline feed of 1000 kg/day. The separation steps were proposed with the main objective of producing and separating hydrocarbons into specific ranges and maintaining low amounts of unwanted components (acylglycerides and unreacted fatty acids). A production capacity of 743.05 kg/day of hydrocarbons was observed in the diesel range, followed by 44.72 kg/day of naphtha and 11.72 kg/day of light hydrocarbons (propane), in addition to other outflows. Process optimization, energy integration and economic feasibility were not evaluated in this work.

Keywords: Hydrotreatment, Vegetable oils, Renewable fuels, Chemical process.

INTRODUCTION

Modern society is still very dependent on fossil fuels. According to , 24 out of 29 European countries studied have fossil fuel energy consumption indicators above 60%, while some of these countries had values above 80%, such as Germany and the United Kingdom. This dependence on non-renewable raw materials (mainly oil) implies potential political, environmental and economic problems at a global level, even more so when it is not known how long the exploitation of this resource will be possible. Martins et al. (2018)

Many alternatives of chemical products and processes have been proposed, such as the use of bioethanol and biodiesel, green hydrogen, fuels produced by Fischer-Tropsch, methanol, DME, hydrocarbons produced by pyrolysis and hydrotreatment of vegetable oils, among others. Among these alternatives, the processes that produce hydrocarbons similar to petroleum have shown great potential,

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[1] State University of Maringá – Paraná
[2] State University of Maringá – Paraná
[3] State University of Maringá – Paraná

since the fuel produced has many similarities to those obtained in the processing of petroleum, and it is possible to directly replace it with little or no adaptation.

The hydrotreatment process of vegetable oils allows the obtaining of renewable hydrocarbons chemically identical to those of petroleum from chemical reactions of deoxygenation. These reactions can transform fatty acids present in the reaction medium into hydrocarbons from three reaction routes: decarbonylation (DCO), decarboxylation (DCO2) and hydrodeoxygenation (HDO). The size of the carbon chain of the hydrocarbons produced varies according to the composition of the vegetable oil fed and the intensity of cracking reactions (dependent on the catalyst and the operating conditions), and it is possible, in a single process, to produce fuels in up to three or four ranges of interest (light hydrocarbons, gasoline, aviation kerosene and diesel). (YANG et al., 2013)

Hydrotreatment can also be performed from a wide variety of catalysts, and noble metals (such as platinum, palladium, ruthenium), transition metals (nickel, molybdenum, cobalt, tungsten) and zeolites are usually used, in addition to the fact that the catalyst support and the active phase of the catalyst can influence its behavior, resulting in even more possibilities of usable catalysts and also significant variations in the selectivities of the reactions involved in the hydrotreatment and/or in the unwanted reactions in the reaction medium of each catalyst (AMEEN et al., 2017; CHEN et al., 2013; DE OLIVEIRA CAMARGO et al., 2020; KUBIČKA; KALUŽA, 2010; MUGHAL, 2011; MURATA et al., 2010; SOTELO-BOYÁS; LIU; MINOWA, 2008; WANG, 2012; ZANDONAI et al., 2016) .

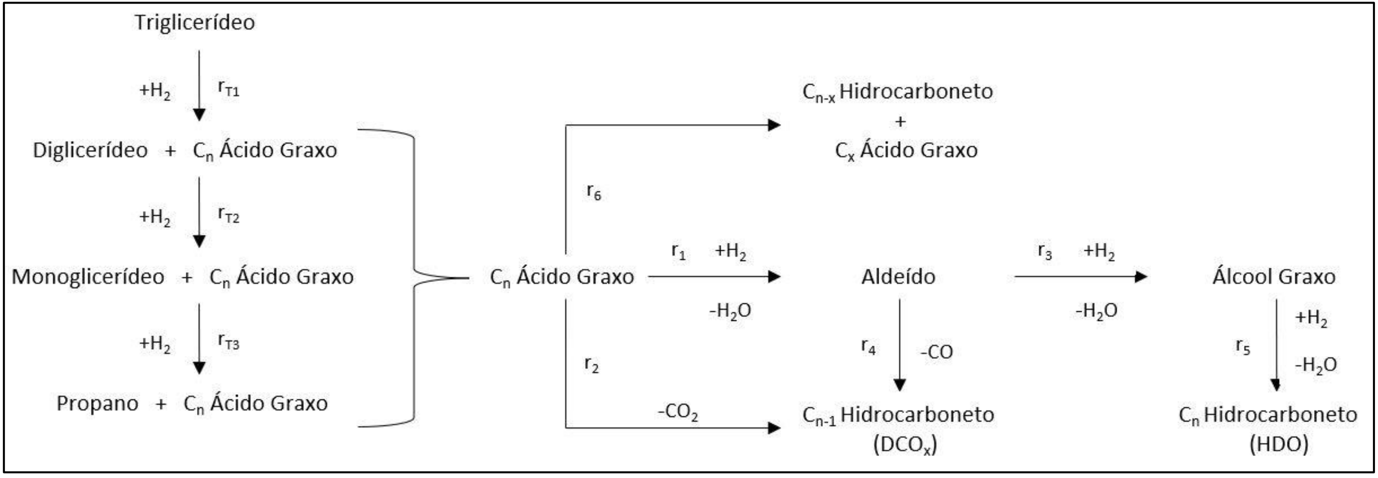
Pepper (2020) synthesized an aerogel catalyst based on nickel and molybdenum carbides supported in gamma-alumina, having found high yields for deoxygenation reactions and a high selectivity of HDO reactions in several experiments using different fatty acids and vegetable oils. The experiments also demonstrated an apparent kinetic behavior close to zero-order for most of the batches tested, and thus the Pimenta-Jorge kinetic model was proposed, based on a Langmuir-Hinshelwood kinetics for the deoxygenation of fatty acids, which is simplified to a model with zero-order behavior in the deoxygenation of pure fatty acids. As for the deoxygenation of vegetable oils, it is necessary to survey some kinetic parameters, however the reactions present a behavior close to the zero order in a good part of the extension of these reactions. Unwanted components, such as coke, were observed in minute amounts, so that no significant catalyst deactivation was observed in sequential trials. (PIMENTA, 2020)

The hydrotreatment tests carried out by presented promising results, and its catalyst was taken as a reference for the realization of this study, proposing the synthesis and simulation of a preliminary chemical process of hydrotreatment of triacylglycerides on a pilot scale, based on a calculation basis of 1000 kg/day of triolein. It was sought to define what will be the necessary transformations, unit operations, operating conditions and yields in a preliminary simulation, in order to obtain renewable diesel from the hydrotreatment of this triacylglyceride in this catalyst. Pepper (2020)

CHEMICAL REACTOR FOR HYDROTREATING TRIOLEIN

The hydrotreatment of triolein follows the Pimenta-Jorge kinetic model (PIMENTA, 2020) for the aerogel catalyst based on nickel and molybdenum carbides supported in alumina. The chemical reactions involved in the transformation of triacylglycerides to linear hydrocarbons can be separated into three groups: hydrogenolysis (r_{t1}, r_{t2}, r_{t3}); Deoxygenation (A)$r_1 r_5$; thermal cracking (r_6). The reaction sequence is described in the Figure 1.

Figure 1 - Triacylglyceride hydrotreatment reactions



Pimenta et al. (2021) observed a very small amount of carbon dioxide being formed in the hydrotreating experiments carried out in the laboratory, and, therefore, did not contemplate the presence of the decarboxylation reaction (DCO2, r_2), and its value is considered null, a fact that is reinforced by other deoxygenation literature based on Ni and NiMo catalysts (ARORA et al., 2019; REDDY YENUMALA; MAITY; SHEE, 2016) **.** Another consideration made is that the reaction rate is much higher than the reaction rate, since no significant concentrations of fatty alcohols were observed throughout the kinetic experiments, so that all fatty alcohol produced is quickly converted into hydrocarbon. $r_5 r_3$ (PIMENTA et al., 2021) Thus, given the kinetic model, one can write the mass balance equations for a PBR reactor as a function of reaction rates (

Table *1*), consumption rates are identified by the negative sign, while production rates are positive.

Table 1 - Mass balances for components involved in the hydrotreatment of triacylglycerides

Component	**Mass Balance**
Triacilglicerídeo	$\frac{d\dot{m}_{TG}}{dW} = -r_{t1}'$
Diacilglicerídeo	$\frac{d\dot{m}_{DG}}{dW} = r_{t1}' - r_{t2}'$
Mono monoaglicerídeo	$\frac{d\dot{m}_{MG}}{dW} = r_{t2}' - r_{t3}'$

Fatty acids	$\frac{d\dot{m}_{AG}}{dW} = r_{t1}' + r_{t2}' + r_{t3}' - r_1' - r_6'$
Aldehydes	$\frac{d\dot{m}_{ALD}}{dW} = r_1' - r_3' - r_4'$
Alcohols	$\frac{d\dot{m}_{ALC}}{dW} = 0$
DCO Products	$\frac{d\dot{m}_{DCO}}{dW} = r_4'$
HDO Products	$\frac{d\dot{m}_{HDO}}{dW} = r_3'$
Cracking Products (Light Hydrocarbons – LHC)	$\frac{d\dot{m}_{LHC}}{dW} = r_6'$

The triacylglyceride considered was triolein, so that the fatty acid formed in its hydrogenolysis is oleic acid. The fatty acid cracking mechanism is considered to occur at the double bond position (ADEBANJO; DALAI; BAKHSHI, 2005; DUPAIN et al., 2007) **,** so that oleic acid cracking tends to form two molecules with 9 carbons (nonane and nonanoic acid). For simplicity, it was considered that the nonanoic acid molecules formed by this cracking were deoxygenated in their entirety, producing nonane. In addition, the reactor considered for the reaction is a packed bed, and considers a fraction of a wet bed (22.5 %) following the results obtained in the drip bed. Finally, the equations of the chemical reaction rates to be implemented in the mass balance are described by the Pimenta-Jorge model, being functions of the specific reaction speed constants, as described in the (PIMENTA, 2020) Table 2.

Table 2 - Expressions of reaction rates considered in the Pimenta-Jorge model for hydrotreatment of triacylglycerides

Reaction rates	Expression
$\boldsymbol{r_{t1}}$	$k_{t1,ap}'C_{TG}$
$\boldsymbol{r_{t2}}$	$k_{t2,ap}'C_{DG}$
$\boldsymbol{r_{t3}}$	$k_{t3,ap}'C_{MG}$
$\boldsymbol{r_{1}}$	$\frac{k_{1,ap}'C_{AG}}{1 + K_{AG}C_{AG}}$
$\boldsymbol{r_{3}}$	$\frac{k_{3,ap}'C_{ALD}}{1 + K_{AG}C_{AG}}$
$\boldsymbol{r_{4}}$	$\frac{k_{4,ap}'C_{ALD}}{1 + K_{AG}C_{AG}}$
$\boldsymbol{r_{6}}$	$k_{6,ap}'C_{AG}$
$\boldsymbol{k_{i,ap}'}$	$k_i'f_w$

The values of the kinetic constants were obtained by adjusting the experimental data performed by Pimenta for the hydrotreatment of soybean oil. Since this oil has most of its composition 18-carbon fatty acids, it was admitted that these parameters would also be suitable for a simplified case with triolein. These values are described in the Table 3.

Table 3 - Kinetic parameters of the specific rates of reactions involved in triolein hydrotreatment provided by Pimenta (2020).

Reaction rates	Value ($^{\text{min-1}}$)	Activation Energy (J.mol-1)
$\boldsymbol{k_{t1}'}$	0,64	2,32 x 104

$\boldsymbol{k_{t2}'}$	1,91	2,80 x 104
$\boldsymbol{k_{t3}'}$	1,1794*	2,10 x 105
$\boldsymbol{k_{1}'}$	0,9292*	4,83 x 104
$\boldsymbol{k_{3}'}$	1,09 x 104	7,46 x 104
$\boldsymbol{k_{4}'}$	7,8 x 103	2,94 x 104
$\boldsymbol{k_{6}'}$	0,039	3,12 x 105
$\boldsymbol{K_{AG}}$	1,81 (adimensional)	

*Data from an adjustment made by the author after verifying inconsistency in the adjustment provided by Pimenta (2020).

With this information, the operation of the chemical reactor up to a point of high hydrocarbon conversions was simulated using the Python programming language. As a reference, a conversion of 99% of triacylglycerides was defined as a reference point for the extension of the chemical reaction, thus defining the operation of the chemical reactor. The operating temperature of the reactor is 380 °C and the pressure is 5 MPa, which are the conditions given as optimal for the hydrotreatment of vegetable oils in the catalyst studied. Considering a feed of 1000 kg/day of triolein, the solution of the differential equation system that reaches the triacylglyceride conversion reference identifies a demand of approximately 22.2 kg of catalyst mass. Under these conditions, the conversions obtained for each component involved in the hydrotreatment are identified in the (PIMENTA et al., 2021) Table 4. These are the parameters used in the simulation of the hydrotreating reactor in the *software* Aspen Plus from RStoic blocos.

Table 4 - Conversions obtained in the simulated concentration profile for the mass balance of the

Table 1

Component	**Conversion**
Triacilglicerídeo	0,98998
Diacilglicerídeo	0,994678
Mono monoaglicerídeo	0,98175
Graxo Acid	0,952751
DCO Product(Heptadecane)	0,37545
HDO (Octadecane) Product	0,524659
Cracking Product (Nonane)	0,052641

The output current of the simulated chemical reactor operating under these conditions has a product distribution described in the Table 5.

The chemical process is synthesized from the operation of this chemical reactor, and the other stages are responsible for feeding reagents, transforming current conditions, separating products, among others.

Table 5 - Distribution of simulated reactor products on Aspen Plus operating at the conversions specified in the Table *1*.

		Mass flow rate (kg/day)	
Component	H2-1	OIL-3	PBR-OUT1
Total	37,975	1000	1037,9750
Triacilglicerídeo		0	10,0200

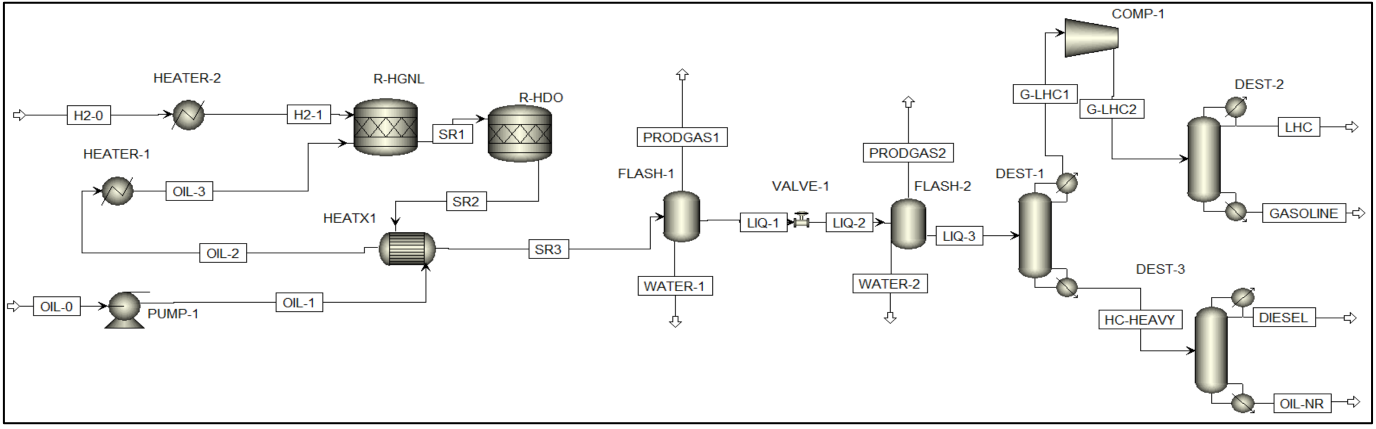
Diacilglicerídeo		0	3,5999
Mono monoaglicerídeo		0	6,5870
Oleic Acid		0	44,3368
Hydrogen	31,56	0	10,4333
Water		0	91,5676
Carbon Monoxide		0	34,9355
n-Heptadecano		0	299,9250
n-Octadecan		0	443,5670
n-Nonan		0	44,8573
Propane		0	48,1449

DESCRIPTION AND SIMULATION OF THE CHEMICAL PROCESS

The synthesized and simulated chemical process, identified in the Figure 2, is powered from two input currents: a triolein current (OIL-0 current) and a pure hydrogen supply current (H2-0 current). The triolein feed stream is pumped (pressure rise up to 5 MPa) and heated to 380 °C using partially the heat from the reactor output streams, arriving at the chemical reactor under the right conditions for the reaction (OIL-3 stream). The hydrogen supply stream, on the other hand, only needs one warm-up, passing through a heat exchanger where it will be heated to the temperature of the reaction (H2-1 current).

Heated and pressurized raw material streams enter the stoichiometric reactors. The first chemical reactor (R-HGNL) considers only hydrogenolysis reactions occurring in series, while the second chemical reactor (R-HDO) considers deoxygenation and thermal cracking reactions occurring in parallel.

Figure 2 - Proposed hydrotreating chemical process



The output current of the second reactor (PBR-OUT1) is used to heat the liquid reactant stream (OIL-1). After that, it has its temperature up to 40 °C with the aid of cold utility, finally reaching the temperature and pressure conditions for the first flash (SR3 current). Next, we have a sequence of flashes and distillations responsible for separating gaseous and liquid products. The flashes separate most of the gaseous product, and much of the volatile gases are removed in the gaseous phases.

The PRODGAS1 and PRODGAS2 streams contain significant amounts of hydrogen and carbon monoxide, and are therefore accounted for as by-products. Here the potential of using these currents in the feedback of the process is highlighted, thus reducing the amount of pure hydrogen fed into the system. In addition, there is potential for the use of these currents in the generation of energy (combustion) or even in a process of reforming the light hydrocarbons present in the currents, thus generating a greater amount of hydrogen that can then be fed back into the system.

The remaining liquid phase passes through a sequence of three simple distillers, simulated using DSTWU blocks, separating the products into three streams: light hydrocarbons (LHC stream); hydrocarbons in the gasoline range (GASOLINE chain); hydrocarbons in the diesel range (DIESEL chain). These separation steps allowed a high degree of purification to be obtained in the product streams, mainly diesel and gasoline, and virtually all acylglycerides and fatty acids were removed from these streams. The chains of final products are arranged in the Table 6.

Finally, the unreacted acylglycerides and fatty acids are removed from the system as a bottom stream in the third distillation column (OIL-NR stream), with a mass flow rate of approximately 65 kg/day, composed mainly of unreacted fatty acids and acylglycerides, as well as hydrocarbons of the diesel fraction that were not separated. It should be noted that this current has the potential to be reused as power supply in the system. The specifications of the unit separation operations are described in the

Table *7*.

Table 6 - Component distribution for simulated chemical process product streams

	Mass flow rate (kg/day)					
Component	PRODGAS1	PRODGAS2	LHC	GASOLINE	DIESEL	OIL-NR
Total	58,9084	25,2748	11,7225	44,7169	743,0476	64,9884
Triacylglyceride	0,0000	0,0000	0,0000	0,0000	0,0000	10,0200
Diacylglyceride	0,0000	0,0000	0,0000	0,0000	0,0000	3,5999
Mono monoacylglyceride	0,0000	0,0000	0,0000	0,0000	0,0000	6,5870
Oleic Acid	0,0000	0,0000	0,0000	0,0000	0,0000	44,3368
Hydrogen	10,1478	0,2839	0,0015	0,0000	0,0000	0,0000
Water	0,2530	0,7039	1,2706	0,0238	0,0000	0,0000
Carbon Monoxide	32,7745	2,1332	0,0278	0,0000	0,0000	0,0000
n-Heptadecano	0,0001	0,0003	0,0000	0,0000	299,9238	0,0011
n-Octadecan	0,0001	0,0001	0,0000	0,0000	443,1234	0,4436
n-Nonan	0,0392	0,1221	0,0036	44,6920	0,0004	0,0000
Propane	15,6936	22,0313	10,4190	0,0010	0,0000	0,0000

Table 7 - Specifications of chemical process separation operations

Unit	Aspen Block	Simulation parameters
FLASH-1	Flash2	Temperature = 40 °C Pressure = 40 bar
FLASH-2		Temperature = 37.96 °C Pressure = 1 bar
DEST-1	DSTWU	Stages = 9 Pressure = 0.5 bar Light -key Recovery = 0,9999 Heavy -Key Recovery = 1E-07
DEST-2		Stages = 6 Pressure = 1 bar Light -key Recovery = 0,9999 Heavy -Key Recovery = 8E-05
DEST-3		Stages = 19 Pressure = 1 bar Light -key Recovery = 0,999 Heavy -Key Recovery = 8E-05

FINAL CONSIDERATIONS

The preliminary chemical process demonstrates a high potential for conversion of triacylglycerides into high molecular weight hydrocarbons. Given a feed of 1000 kg/day of triolein and a catalyst mass of 22.2 kg, approximately 77.02 % of the mass of reactants fed into the system were separated into streams of light hydrocarbons, gasoline or diesel products (LHC, GASOLINE and DIESEL streams). In addition, two streams of gaseous products were produced with significant amounts of hydrogen, carbon monoxide and propane (streams, PRODGAS1 and PRODGAS2), which represent 8.11 % of the mass of reagents fed, and approximately 6.26 % of the initial mass fed did not react in the process and could be reused or recycled.

An important point to be emphasized is that the streams of gaseous products would have a different composition if there was a presence of methanation reactions in considerable quantity, which were not represented in the system since there is no kinetic information of this reaction for the catalyst under the conditions studied. Another possibility, in case of methanation present in significant quantities, would be the use of methane produced as a source of thermal energy (combustion) or even as raw material, together with the propane produced in hydrogenolysis reactions, for the production of hydrogen from a possible methane/propane reforming process.

The separation steps proved to be effective, so that the main hydrocarbon products were separated into distinct carbon chain bands, presenting a high degree of purity of these fuels and almost zero amounts of fatty acids or acylglycerides in their composition. The light hydrocarbon stream (LHC) has a significant amount of water that must be removed during distillation (DEST-2).

It is worth mentioning that, as it is a preliminary process, operating conditions that were consistent with the process up to the separation of linear hydrocarbons were considered, leaving the implementation of recycles, process optimization, complete energy integration and economic analysis for another time, since there are still many variables to be studied and analyzed. It is also believed that other processes such as hydrocarbon isomerization or the use of reforms for hydrogen production can be associated with the developed process, and are also the target of future studies.

In addition, a preliminary, direct and simplified process of hydrotreatment of a representative triacylglyceride for diesel production was demonstrated. Other products, such as aviation kerosene or even gasoline can be obtained as main products from vegetable oils with fatty acids of lower chains. Processes using blends of oils can theoretically also be used, however they will present specific problems and, therefore, will require modifications in the chemical process.

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REFERENCES

Adebanjo, A. O., Dalai, A. K., & Bakhshi, N. N. (2005). Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat. Energy and Fuels, 19(4), 1735–1741. https://doi.org/10.1021/ef049974s

Ameen, M., et al. (2017). Catalytic hydrodeoxygenation of triglycerides: An approach to clean diesel fuel production. Renewable and Sustainable Energy Reviews. Elsevier Ltd. https://doi.org/10.1016/j.rser.2017.04.004

Arora, P., et al. (2019). Kinetic study of hydrodeoxygenation of stearic acid as a model compound for renewable oils. Chemical Engineering Journal, 364, 376–389. https://doi.org/10.1016/j.cej.2019.01.059

Chen, W., et al. (2013). Effect of modification of the alumina acidity on the properties of supported Mo and CoMo sulfide catalysts. Journal of Catalysis, 304, 47–62. https://doi.org/10.1016/j.jcat.2013.04.003

De Oliveira Camargo, M., et al. (2020). Green diesel production by solvent-free deoxygenation of oleic acid over nickel phosphide bifunctional catalysts: Effect of the support. Fuel, 281, 118604. https://doi.org/10.1016/j.fuel.2020.118604

Dupain, X., et al. (2007). Cracking of rapeseed vegetable oil under realistic FCC conditions. Applied Catalysis B: Environmental, 72(1–2), 44–61. https://doi.org/10.1016/j.apcatb.2006.12.023

Kubička, D., & Kaluža, L. (2010). Deoxygenation of vegetable oils over sulfided Ni, Mo, and NiMo catalysts. Applied Catalysis A: General, 372(2), 199–208. https://doi.org/10.1016/j.apcata.2009.12.029

Martins, F., Felgueiras, C., & Smitková, M. (2018). Fossil fuel energy consumption in European countries. Energy Procedia. Elsevier Ltd. https://doi.org/10.1016/j.egypro.2018.03.104

Mughal, A. A. (2011). Hydrogenation of vegetable oil over NiMo-S/γ-Al2O3, Pt/β-Zeolite & Pd/C catalysts for biodiesel production. Göteborg. https://doi.org/10.1111/j.2040-8765.2011.00001.x

Murata, K., et al. (2010). Production of synthetic diesel by hydrotreatment of jatropha oils using Pt-Re/H-ZSM-5 catalyst. Energy and Fuels. https://doi.org/10.1021/ef100065p

Pimenta, J. L. C. W. (2020). Production of hydrocarbons similar to petroleum derivatives from the hydrotreatment of vegetable oils (Doctoral dissertation, State University of Maringá, Maringá).

Pimenta, J. L. C. W., et al. (2021). A novel kinetic model applied to heterogeneous fatty acid deoxygenation. Chemical Engineering Science, 230, 116087. https://doi.org/10.1016/j.ces.2021.116087

Reddy Yenumala, S., Maity, S. K., & Shee, D. (2016). Reaction mechanism and kinetic modeling for the hydrodeoxygenation of triglycerides over alumina supported nickel catalyst. Reaction Kinetics, Mechanisms and Catalysis. https://doi.org/10.1007/s11144-016-1036-8

Sotelo-Boyás, R., Liu, Y., & Minowa, T. (2008). Production of green diesel by hydrocracking of canola oil on Ni-Mo/γ-Al2O3 and Pt-zeolitic based catalysts.

Wang, H. (2012). Biofuels production from hydrotreating of vegetable oil using supported noble metals, and transition metal carbide and nitride. Available at: http://digitalcommons.wayne.edu/oa_dissertations

Yang, Y., et al. (2013). Hydrotreating of C18 fatty acids to hydrocarbons on sulphided NiW/SiO2-Al2O3. Fuel Processing Technology, 116, 165–174. https://doi.org/10.1016/j.fuproc.2013.06.015

Zandonai, C. H., et al. (2016). Production of petroleum-like synthetic fuel by hydrocracking of crude soybean oil over ZSM5 zeolite - Improvement of catalyst lifetime by ion exchange. Fuel, 172, 228–237. https://doi.org/10.1016/j.fuel.2016.01.017