EVALUATION OF PT/MWCNT AS CATALYST TO PRODUCE BIO-HYDROCARBONS FROM POULTRY VISCERA OIL

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ABSTRACT

Drop-in biofuels are composed by synthetic bio-hydrocarbons and are the only alternative to substitute fossil jet fuel, since they can meet to rigid specifications required to aviation fuels. This type of biofuels can be produced by different routes. Hydroprocessing can produce bio-hydrocarbons from vegetable oils and animal fats, in the presence of a catalyst, at high temperatures and pressures. The efficiency and cost of this process is related to the utilization of an efficient catalyst and a cheap raw material. In this work, it was investigated the utilization of a carbon nanotube supported platinum (Pt/MWCNT) catalyst to convert poultry viscera oil, a waste from chicken meat production, into bio-hydrocarbons. The results of reactions with 5 wt% of catalyst, at 350 °C and under 30 bar H_2 showed the Pt/MWCNT efficiency to promote deoxygenation reactions, while MWCNTs appear to have catalytic activity to triglycerides cracking reactions. Therefore, the use of this nanocatalyst and poultry oil seems to be a promising alternative to produce biojet fuels. However, to achieve higher degree of deoxygenation, it is necessary to study the influence of some process variables, such as pressure, time reaction and H_2/raw material ratio.

Keywords: bio-hydrocarbons, drop-in biofuels, deoxygenation, poultry oil, carbon nanotubes.

1. INTRODUCTION

Currently, several industrial sectors are prioritizing the utilization of clean and renewable energies, as a way to achieve a sustainable development and a reduction of pollutants emission, such as carbon dioxide. The civil aviation sector has shown a big interest and necessity of replacing fossil kerosene by a biofuel, according to the targets established by Carbon Offsetting and

Reduction Scheme for International Aviation (CORSIA/ICAO) (DE SOUZA; MENDES; ARANDA, 2018; ICAO, 2017). In this context, bio-hydrocarbons or drop-in biofuels are the substitutes to fossil jet fuel, since these compounds are chemically similar to fossil fuels and, as a result, can present physic-chemical properties that are specified for jet fuels, such as low freezing point and high heat content (SILVA et al., 2016).

The production of bio-hydrocarbons from biomass can occur by different routes, such as hydroprocessing of esters and fatty acids (HEFA), in which vegetable oils and/or animal fats can be deoxygenated in the presence of a catalyst, at high temperatures and hydrogen pressures (CHOUDHARY; PHILLIPS, 2011; GUTIÉRREZ-ANTONIO et al., 2017). One of the biggest challenges of biojet fuel production is to obtain a product with competitive prices, which demands inexpensive feedstock and efficient process (WANG; TAO, 2016). Residual fats are relevant raw materials to produce bioproducts, according to their sustainable character and low cost. Considering that Brazil is the second biggest chicken producers of world, there is a big availability of triglycerides that can be converted into biofuels, such as biojet fuel (ABPA, 2018). Therefore, in this work it was proposed the utilization of a carbon nanotubes supported platinum catalyst to synthetize bio-hydrocarbons from poultry viscera oil. This feedstock presents high sustainability and industrial interest.

2. METHODS

2.1 Synthesis and characterization of catalyst

The catalyst was synthetized and supplied by Laboratory of Nanomaterials/Department of Physics of Universidade Federal de Minas Gerais. The multi-walled carbon nanotubes (MWCNTs) were synthetized by catalytic chemical vapor deposition, over a magnesium oxide supported cobalt/iron catalyst. The main properties of these MWCNTs are presented in table 1.

Table 1. Properties of MWCNTs utilized as support of catalyst.

Property	Value
Nanotubes purity	> 93%
Other carbon structures	< 2%
Impurities	< 5% (catalyst Co-Fe/MgO residue)
Major outer diameter	10 nm – 50 nm
Estimated length of tubes	5 μm – 30 μm

The final catalyst (Pt/MWCNT) was obtained by wet impregnation, using platinum hexachloride solution. After this, the impregnated platinum was reduced using hydrazine in magnetic stirrer.

2.2 Poultry/chicken oil characterization

The poultry/chicken viscera oil was supplied by the enterprise Patense (MG). Table 2 presents some chemical properties informed by the company.

Table 2. Chemical properties of poultry/chicken viscera oil.

Property	Value (%wt)
Humidity	< 0.5
Impurity	< 0.5
Acidity free in oleic acid	2.5 – 5.0
Unsaponifiables	< 0.5
Total fatty acids	> 97.0

Source: PATENSE, 2019

The oil also was characterized by mid-infrared spectroscopy (IR), using Nicolet iS5 FTIR spectrometer from ThermoFisher in zinc selenide cell by attenuated total reflectance Fourier-transform infrared. The measurements were performed with 32 scans and resolution of 4 cm^{-1}. Furthermore, fatty acid profile was determined by gas chromatography with flame ionization detector (GC-FID), in compliance with the standard DIN EN 14103 (GERMAN INSTITUTE OF STANDARDIZATION, 2011). The analyses were performed in a gas chromatography GC-2010 Shimadzu with an automatic sampler AOC-20i. Identification of peaks and quantification were made using the standard SUPELCO37® from Sigma-Aldrich.

2.3 Catalytic deoxygenation reactions

Prior to reactions, the catalysts, Pt/MWCNT and MWCNT, were dried in a muffle furnace for 2 h at 400 °C. Furthermore, both catalysts were reduced *in situ* in a batch reactor Parr 4348, with a 100 mL vessel, under 5 bar of H_2, at 250 °C for 2 hours. For each reaction, 1.25 g of catalyst were used (5 %wt). Then, 25 g of raw material were added to reactor, which was initially pressurized with 30 bar H_2. After, the reactions were conducted at 350 °C for 3 hours. Reactions at the same experimental conditions, but in the absence of catalysts, were performed for comparative purpose (blank reactions). Table 3 presents the codes for all performed reactions.

Table 3. Variable conditions and respective codes for the reactions performed under 30 bar of H_2, at 350 °C for 3 h.

Raw material	Catalyst	Reaction Code
Poultry oil	MWCNT	PO-CNT
Poultry oil	Pt/MWCNT	PO-PtCNT
Poultry oil	Blank	PO-B
Oleic acid	MWCNT	OA-CNT
Oleic acid	Pt/MWCNT	OA-PtCNT
Oleic acid	Blank	AO-B

2.4 Characterization of products

The synthetized products were characterized by mid-infrared spectroscopy using Nicolet iS5 FTIR spectrometer from ThermoFisher in zinc selenide cell by attenuated total reflectance Fourier transform infrared. The measurements were performed with 32 scans and resolution of 4 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 Poultry/chicken oil characterization

The infrared spectrum of chicken oil is presented in next section (3.2), to be used for comparison with products of reactions. The results for the fatty acid profile are shown in Table 4.

Table 4. Fatty acid profile of poultry/chicken oil.

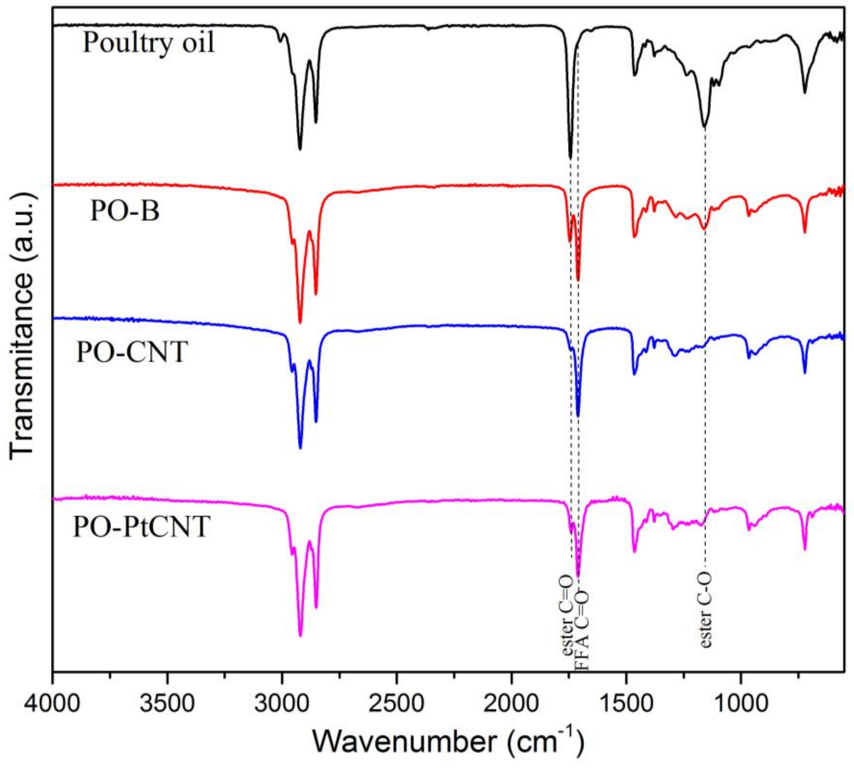
Fatty acid		Composition (%wt)
Common name	**Notation**	
Myristic acid	C14:0	0.45
Myristoleic acid	C14:1	0.08
Palmitic acid	C16:0	22.31
Palmitoleic acid	C16:1	4.27
Stearic acid	C18:0	1.05
Oleic acid	C18:1	43.58
Linoleic acid	C18:2	25.16
Arachidic acid	C20:0	0.24
Linolenic acid	C18:3n6	1.69
Eicosadienoic acid	C20:2	0.16
Eicosatrienoic acid	C20:3n3	0.22
Others		0.79
Saturated compounds (%wt)		24.05
Unsaturated compounds (%wt)		75.16

It can be observed that the poultry oil is mainly composed of oleic acid (C18:1), linoleic acid (C18:2) and palmitic acid (C16:0). Besides that, the oil presented high amount of unsaturated fatty acids (75.16 %wt), which is relevant to hydroprocessing reactions, since it can lead to higher consumption of H_2 and higher occurrence of cracking/isomerization reactions (PATTANAIK; MISRA, 2017).

3.2 Catalytic deoxygenation reactions

The study of deoxygenation performance of the proposed catalysts was made by a qualitative analysis of infrared spectra of reactants and reactions products. For this purpose, bands related to oxygenated groups, such as carbonyl and ester groups, were observed to measure the degree of deoxygenation of each reaction. The spectra for poultry oil and its products are presented in Figure 1.

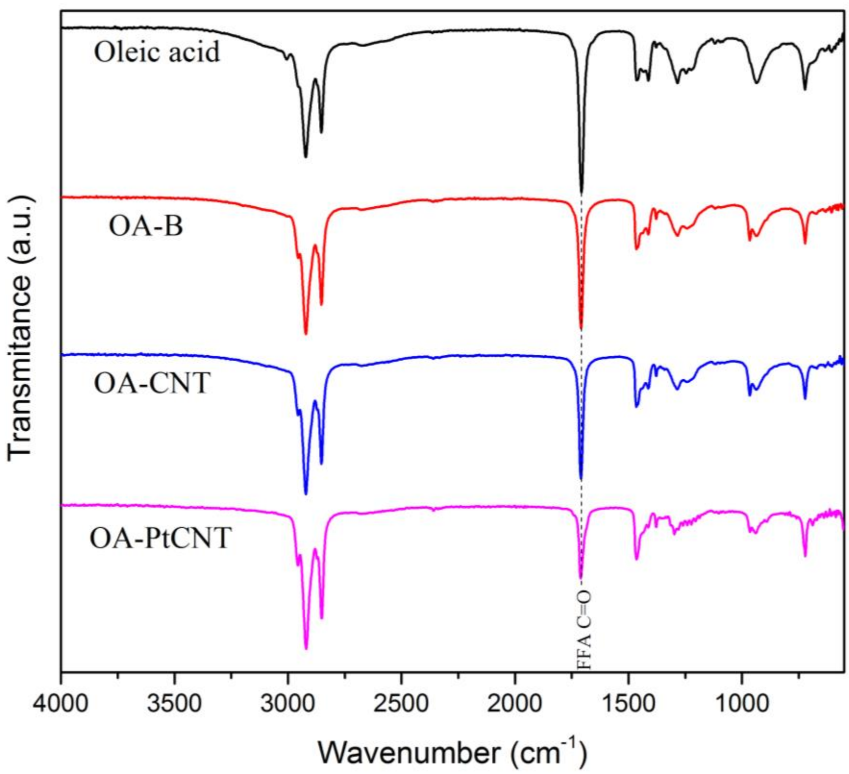
Figure 1. Infrared spectra of reactant and products obtained using poultry oil as raw material.



It can be observed a considerable decrease of ester related bands (1740 cm^{-1} and 1160 cm^{-1}) in both reactions with catalysts, while this reduction was not so intense for blank reaction (PO-B). However, it was not achieved the total conversion of triglycerides including the reactions with catalysts. As a consequence of the triglycerides hydrogenolysis reactions, a band related to carbonyl group from carboxylic acid (1710 cm^{-1}) appears in the spectra of all reaction products. It can be observed that the spectrum of product PO-PtCNT has the less intense band related to oxygenated groups, which indicates to a higher degree of deoxygenation using Pt/MWCNT catalyst.

Aiming to understand better the performance of the catalyst for deoxygenation reaction, it was used a model compound, the oleic acid, feedstock. As shown in Table 4, it is the main compound of the poultry fatty material. The better performance observed for the catalyst with platinum can be confirmed by analysis of spectra of reactions products obtained by using oleic acid as precursor, presented in Figure 2.

Figure 2. Infrared spectra of reactant and products of reactions using oleic acid as raw material.



It is possible to affirm that the catalyst Pt/MWCNT has a great activity for deoxygenation reaction, since it can be observed a considerable difference between intensities of carboxyl group band (1710 cm^{-1}) in spectra of reactions products, being the less intense band related to OA-PtCNT-3 product. Furthermore, it is possible to affirm that the presence of platinum is crucial for deoxygenation, since that in the absence of this metal it was not observed a considerable decrease in carboxyl band intensity. However, spectra presented in Figure 1 showed that the MWCNTs promoted similar degree of triglycerides hydrogenolysis when compared with Pt/MWCNT. Therefore, it can be stated that MWCNTs are efficient to promote the conversion of triglycerides into free fatty acids, while the platinum presents activity to promote the deoxygenation of these fatty acids into hydrocarbons.

Even that Pt/MWCNT catalyst has efficiency to produce bio-hydrocarbons, for both reactions using this catalyst, PO-PtCNT-3 and OA-PtCNT-3, it was not achieved a total degree of deoxygenation, which is evidenced by the presence of oxygenated groups related bands in the products spectra. These data are probably due to insufficient time of reaction or low H_2/raw material ratio, variables that can restrict the occurrence of deoxygenation in higher levels. Further studies to optimize the reaction parameters must be carried out to maximize the bio-hydrocarbons yields.

4. CONCLUSIONS

The current study allowed the evaluation of Pt/MWCNT utilization as catalyst to produce bio-hydrocarbons from poultry oil. It was possible to identify the catalyst support (MWCNTs) activity to promote triglycerides cracking and the catalytic activity of Pt/MWCNT for deoxygenation of fatty acids. However, it was not possible to achieve a total degree of deoxygenation in the experiments conducted in this study. According to what was observed, it will be necessary to carry out more reactions to evaluate the influence of some variables, such as time reaction, pressure and H_2/raw material molar ratio, aiming to obtain higher yield in bio-hydrocarbons. Hence, it can be concluded that Pt/MWCNT is a potential nanocatalyst to synthetize drop-in biofuels from oils and fatty acids. Furthermore, the poultry oil appears as an alternative to usual sources of fatty compounds, since it presents low cost and high availability, mainly in Brazil.

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