Definition of the Catalyst Family for the Production of Green Diesel by Hydrotreatment \textit{In Situ} of Triglycerides

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As an alternative to the use of conventional biodiesel, a good number of researches have been carried out searching for a more similar green diesel to fossil diesel. The most promising route at the commercial level to produce it is by hydrotreatment of oleaginous biomass, which breaks large molecules (such as triglycerides) through the catalytic action of hydrogen and removes oxygen atoms (deoxygenation) and other elements that are not carbon and hydrogen. However, using hydrogen gas at high pressure to solubilise it in the liquid phase makes the process lose sustainability, since at least 90 \% of the hydrogen comes from non-renewable sources. One of the possible solutions to this issue is the use of a biodonor that generates the hydrogen required in the process and transfers it catalytically to the substrate that is aimed to be hydrotreated. As additional advantages, a reduction in the operating pressure and improved catalyst stability can be achieved. The following work aims to find the most appropriate catalyst for the process of deoxygenation of oleaginous biomass with hydrogen generation \textit{in situ}, considering that it must promote the generation of hydrogen by catalytic transfer and at the same time it should favour the deoxygenation of triglycerides (it must be bifunctional). By means of a multicriteria decision algorithm (Macbeth method), a group of catalysts is selected from five families (transition metal sulphides, metal carbides, nitrides and phosphides, reduced noble metals, and reduced transition metals) with five criteria (preparation-acquisition, bifunctionality-selectivity, cost-availability, hydrogen dissociation and stability-useful life). Then, within the selected family, possible catalysts are chosen according to the review carried out considering physicochemical aspects of the interaction of the molecules with the surface. For this process, the most promising catalysts are noble metals, mainly Pd/C.

1. Introduction

For almost 20 years, biofuels have appeared commercially on the world’s scenario as one of the measures to reduce climate change and to reduce greenhouse gas emissions through the partial or total replacement of fossil fuels used mainly in ground transportation. However, the first biofuels used, called the first generation, have presented many drawbacks and are still not fully sustainable. In the case of diesel fuel, the modification of an existing technology can result in a greater energy cost than that generated by the innovative energy source. In other words, to be viable the net energy of the fuel must be positive. Some research have studied the production of biodiesel (Bezergianni & Dimitriadis, 2013). For example, Hill et al. (2006) made a life cycle assessment and concluded that biodiesel produces 93 \% more energy than the energy it consumes in its production process and reduces greenhouse gases by 41 \%. In addition, they argue that biodiesel is more economically competitive than bioethanol, and it is expected that in the future, with the depletion of oil reserves, compete with fossil fuels (Hill et al., 2006). Traditional biodiesel, obtained by methyl esterification of fatty acids (FAME), has low storage stability and poor cold flow properties, is excessively solvent, has compatibility problems with the engine, and hinders the formation of a stable mixture with the fossil diesel when its concentration is higher than 5 \% (Kalnes et al., 2008).

As an alternative solution to the environmental, social and technical disadvantages of first-generation biofuels, and based on the concept of biorefinery, a large amount of research has been carried out on the production of
other alternatives, unconventional, and advanced biofuels. For conventional biodiesel, there are other options that are more sustainable than the non-ester type, but these are not very common. One of these options is the green diesel, GD, which is produced mainly by hydrotreating vegetable oils. GD is a very similar fuel to fossil diesel and can replace it completely (Mayorga et al., 2019). It also has thermal and reactive stability, and does not contain oxygen. In addition, it can be obtained from a wide range of raw materials, being an alternative to traditional transesterification (Lindfors, 2010).

Equation (1) is the global reaction of a triglyceride of vegetable oil to n-alkanes, which are the main components of the GD:

\[
\text{Triglycerides} + H_2 \rightarrow \text{Normal Alkanes (C11 to C-18 mainly)} + CH_4 + C_3H_8 + H_2O + CO_2 + CO
\] (1)

However, this reaction is not precise enough for presenting each of the chemical mechanisms by which oxygen is removed to generate the normal hydrocarbons. Two reactions in competition appear specifically in this process: hydrodeoxygenation - HDO (Eq. 2) and decarboxylation - DCX (Eq. 3) of the fatty acids, which are intermediates generated after the saturation and rupture of the triglyceride by the hydrogen.

\[
\text{RCOOH} + 3H_2 \rightarrow \text{RCH}_3 + 2H_2O
\] (2)

\[
\text{RCOOH} \rightarrow \text{RH} + \text{CO}_2
\] (3)

The catalyst plays an important role because it must lead the route of the deoxygenation process (Romero et al., 2018). However the production of GD requires gaseous hydrogen at high pressure (for solubilization in liquid phase), which is very hazardous and of complex handling, besides its commercial origin that is fossil in more of 90 % at world level. The solution to the last problem in the production of GD is that the hydrogen can be replaced by a biodonor, which generates the hydrogen in situ by catalytic transfer (CTH), so the catalyst employed in the deoxygenation process of the triglyceride must be able to do this. In other words, the catalyst for the production of GD by in situ hydrotreatment has a double function. First, it generates hydrogen from the donor (M.A. Mayorga et al., 2020) and, second, it must use the hydrogen for the reduction of the triglycerides to GD. In general, the most economical catalysts, with high selectivity towards deoxygenation, and, therefore, the most used in the hydrotreatment of oil are bimetallic sulphides, since the presence of metals in the sulphide phase increases the basicity of sulfide anions (Brillouet et al., 2014). However, they have drawbacks due to the presence of sulfur, as their leaching and subsequent loss of the active phase when used for long periods of time causes the notorious deactivation of the catalyst and, consequently, the contamination of the obtained liquid products of interest (Kubička & Horáček, 2011). Research on the supports can give light on the resolution of this problem. Also, metal phosphide and carbide catalysts have shown high selectivity to produce aliphatic alkanes, but their complex preparation and the activation of the active phase have shown their short shelf life, which is not favourable for the long-term process (Srifa et al., 2015). Figure 1 shows the different components used in the catalytic systems employed in hydrotreatment. Several of them, both of active phase and support, have been used as a catalyst in hydrogen generation by CTH.

As discussed above, the catalyst selected in this type of process plays a fundamental role in favouring the hydrodeoxygenation reaction. In the classification of heterogeneous catalysts for the hydrogenation reaction, both metals and semiconductor oxides can be used (Bond, 1987). The active component for a redox hydrogenation reaction must be conductive like a metal (for example Fe, Ni or Pt), while for a selective hydrogenation (redox) it must be semiconductor, as an oxide or sulfide (e.g., NiO, ZnO, CuO) (Richardson, 1992). For a redox hydrogenolysis, the active component can be a conductor such as a metal (e.g., Pd, Cu, Ag) or a semiconductor such as an oxide or sulphide (Cr₂O₃, MoS₂). Metal catalysts are also recommended for reactions involving hydrogen as hydrogenation and hydrogen adsorption.
The catalysts used in hydrotreatment of oils are mainly metals and sulfurized bimetallic compounds, which may or may not be supported. The main factor to consider for the design of the catalyst is which of the two reactions (HDO or DCX) you want to prioritise. The DCX reaction is favoured by metal catalysts, such as Co, Pd, Pt, Ni, Rh, Mo and Ru, where cobalt is the compound with the highest catalytic activity. It has been observed that the use of Pd, Pt and Ni strongly promotes the methane reaction, increasing H2 consumption. On the other hand, HDO is favoured mainly by metals, such as V, Fe and W, which have a special affinity, as they reduce the temperature conditions, increase the conversion and improve the selectivity towards the saturated alkanes that constitute the final product. For HDO, preference is also given to sulfur bimetallic compounds (Ni/CoS2, CoMoS2 and NiWS2). The main problem of these catalysts is their instability in the reactive medium and the leaching of sulfur, therefore, one of the most used alternatives is to support them on matrices of γ-Al2O3, to increase the stability. Within these catalysts, Ni/CoS2 and CoMoS2 are especially important as they have a high selectivity towards HDO and can operate at a lower temperature due to the exothermic nature of the reaction (Srifa, et al., 2014). In contrast, the saturation of the double bonds is more easily carried out using the Pd and Pt catalysts (Ki et al., 2014).

This work aims to select the most suitable catalyst for the GD production process by in situ hydrotreatments of triglycerides. So, five families of catalyst phases are considered: (i) reduced noble metals, (ii) reduced transition metals, (iii) mono and bimetallic sulphides, (iv) metal carbidies, phosphides and nitrides, and (v) polyacids, oxides, salts and PILC. With the MACBETH algorithm, the family of catalysts is selected using five criteria: (i) preparation-acquisition, (ii) bifunctionality-selectivity, (iii) cost-availability, (iv) hydrogen dissociation and (v) stability-useful life. Finally, according to the selected family, the research proceed to review which are the characteristic catalysts of this family. As a result, considering physicochemical aspects such as molecule-surface interaction, the most suitable catalysts will be chosen for the process.

2. Methodology

According to the theory of utility, each criterion provides a partial description of the global utility of each of the alternatives. Therefore, the global utility can be calculated from the partial profits, using a linear combination of weights and functions obtained from valuations of experts, according to Eq. (4):

\[ U_i = \sum_{j=1}^{n} w_j f_j(C_j) \]  

where \( U_i \) is the utility of the alternative \( i \), \( w_j \) is the weight of the criterion \( j \) (n criteria) and \( f_j(C_j) \) is a function of preference for each criterion \( j \). The main difference of Macbeth with other multicriteria methods is that, to generate the scores of the options and weigh the criteria, only qualitative judgments of attractiveness difference are required between the criteria. So, the method allows establishing semantic categories of different attractiveness: null, very low, low, moderate, strong, very strong and extremely strong. Once the criteria to evaluate the alternatives have been selected, as a first step experts should order them from highest to lowest, according to the importance of each criterion for the final result. Then, they must give the numerical value that separates an alternative from the one immediately following, taking into account only two criteria at the same time. Likewise, the last criterion must be compared with a non-existent one that have no importance in the catalyst. The weight, \( w_j \), is obtained with the differences \( a_{jk} \) between criterion \( j \) and criterion \( k \), according to Eq. (5). After with \( w_j \) and the function for each criterion, using Eq. (4) the utility \( U_i \) is determined and the set of alternatives are ordered from highest to lowest. This final order is used for decision making.

\[ w_j = \frac{\sum_{j=1}^{n} a_{jk} - \sum_{j=1}^{n} a_{jk}}{\sum_{j=1}^{n} a_{jk} - \sum_{j=1}^{n} a_{jk}} \]  

The main challenges to overcome in the design of catalysts are those related to its stability, selectivity and activity, as well as its availability and low cost. These aspects must, therefore, be contained in the established criteria. To give a rating on each criterion, information such as the following is available: comparison in terms of cost, preparation, bifunctionality, activation energy for dissociation, and deactivation pathways between the active components of the catalysts (metallic or bimetallic sulphides, metallic carbidies, nitrides or phosphides and reduced metals) used in hydrotreatment. It can be seen in Table 1 that the routes of deactivation are related to the stability-useful life criteria. Since replacing and regenerating a catalyst is costly for the industry, stability must be improved, and the useful life of the catalysts used must be increased (Patel & Kumar, 2016). Another option is the search for cheaper and well-behaved catalysts (Kloprogge, et al., 2005).
Table 1: Comparison among catalysts for hydrotreatment. Adapted from (Ruddy et al.).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Metallic or Bimetallic Sulphides</th>
<th>Metallic Carbons, nitrides or phosphides</th>
<th>Reduced Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Intermediate</td>
<td>High</td>
</tr>
<tr>
<td>Preparation</td>
<td>Low-intermediate</td>
<td>Intermediate-high</td>
<td>Low</td>
</tr>
<tr>
<td>Selectivity</td>
<td>HDO</td>
<td>HDO</td>
<td>DCX</td>
</tr>
<tr>
<td>Bifunctionality</td>
<td>Saturated plane and active sites (S-H) for hydrogenation</td>
<td>Oxygen modifies sites (-OH)</td>
<td>Metal sites for hydrogenation</td>
</tr>
<tr>
<td>Activation energy for dissociation of</td>
<td>0.55-0.97 eV MoSx</td>
<td>0.00 eV MoP(001)</td>
<td>0.12 eV Pd(111)</td>
</tr>
<tr>
<td>H₂</td>
<td>0.32-0.74 eV NiMoSx</td>
<td></td>
<td>0.00 eV Ru (0001)</td>
</tr>
<tr>
<td>Routes of deactivation</td>
<td>Surface oxidation</td>
<td>Surface oxidation</td>
<td>Sintering</td>
</tr>
<tr>
<td>Leaching of S</td>
<td>Coke generation</td>
<td>Loss of C / N / P</td>
<td>Sulfur poisoning</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Through the MAUT for each of the criteria defined below, the weight \( w_j \) is determined by observing how big is the difference between the five criteria presented, organised from the most to the least important: (1) preparation-acquisition, (2) bifunctionality-selectivity, (3) cost-availability, (4) hydrogen dissociation and (5) stability-useful life and (6) other possible. With these evaluations, in Table 2 the difference between the row criterion and the column criterion is placed, to calculate \( w_j \) for each criterion, according to Eq. (5).

Table 2: Calculation of the weight assigned to each criterion.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>j</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>( \Sigma )</th>
<th>Difference</th>
<th>Relative ( w_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation-Acquisition</td>
<td>1</td>
<td>-</td>
<td>17</td>
<td>8</td>
<td>8</td>
<td>11</td>
<td>17</td>
<td>61</td>
<td>11</td>
<td>1.0000</td>
</tr>
<tr>
<td>Bifunctionality-Selectivity</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>11</td>
<td>11</td>
<td>14</td>
<td>50</td>
<td>8</td>
<td>0.8197</td>
</tr>
<tr>
<td>Cost-Availability</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>17</td>
<td>17</td>
<td>42</td>
<td>11</td>
<td>0.6885</td>
</tr>
<tr>
<td>Hydrogen dissociation</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>17</td>
<td>31</td>
<td>11</td>
<td>0.5082</td>
</tr>
<tr>
<td>Stability-Useful life</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>20</td>
<td>0.3279</td>
</tr>
<tr>
<td>Others</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \Sigma )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td>3.3443</td>
</tr>
</tbody>
</table>

For the qualifications of each alternative (presented in Table 3), technical justifications were taken into account in each criterion. Now, by the Macbeth method, the utility is calculated from the rating of 10 for each criterion \( j \) for each alternative \( i \), according to Eq. (4), whose results are shown in Table 3.

Table 3: Calculation of the global utility for each alternative.

<table>
<thead>
<tr>
<th>Alternative, ( i )</th>
<th>Criteria, ( j )</th>
<th>( U_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced noble metals</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Reduced transition metals</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Polycarboxylic, oxides, salts, PILC</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Mono and bimetallic sulphides</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Metal carboxylics, phosphides and nitrides</td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>

According to the previous multicriteria analysis, it is observed that the alternatives that have a global utility over 10, greater than 7 in descending order are reduced noble metals and reduced transition metals. Within these selected families, the following options are taken into account:
- Reduced noble metals: Pt, Pd, Rh, Ru, Go, Os
- Reduced transition metals: Ni, Mo, W, Co, Fe, Cu

As the catalyst will control the selectivity in each of the feasible decompositions, it is important to consult the Volcano diagram of the reaction that generates hydrogen, which allows the choice of the most appropriate catalyst. For example, regarding the decarboxylation of formic acid that allows the generation of hydrogen, the Volcano diagram in Figure 2 indicates that, concerning transition metals, the most appropriate catalysts for this reaction are noble metals, such as Ru, Rh, Pd, Pt and Ir. Metal catalysts have emerged thanks to their high reactivity to produce aliphatic alkanes from triglycerides. In turn, they have the advantage of working at moderate conditions for the other alternatives and use less excess of hydrogen for the reaction.
Generally, depending on the catalyst used, deoxygenation can be selective or non-selective. In the selective, GD is generated as the main product, for which supported catalysts such as noble metals or bimetallic sulphides are used. Noble metals are characterised by their high selectivity and low H₂ consumption, and for favouring DCX. H₂ is only necessary to saturate olefin compounds and stabilise the catalyst and Pd/C is a promising catalyst for industrial applications due to its high activity and selectivity (Hachemi et al., 2017). A solid catalyst that resists coking, high water concentration and poisoning, and that can be easily regenerated without losing too much activity, is highly desired for the HDO process (He & Wang, 2012). The vast majority of authors express the need to do more research in the area of catalyst regeneration and recycling to increase their useful life, especially in the case where the starting raw material has many components to carry out the hydroprocessing (Arun et al., 2015). Additionally, the generation of products such as water during biomass HDO, in addition to coke, has, in many cases, led to catalyst deactivation, which requires the search for more stable catalysts (Mortensen et al., 2015).

It is necessary to consider against the selection of the support that the rupture increases with the acidity of the catalysts and that the reactions are highly exothermic (both the reaction of H₂ generation by formic acid, and the reactions of HDO and DCX), since the stability of the catalyst is important (Anand & Sinha, 2012). Diversity of supports are shown in Figure 1, but for catalysts of metallic type, there is a preference for supports with an acidic character, thus zeolites and alumina are the most commonly used supports compared to those of a basic or neutral nature, as this favours the mechanisms involved. Good yields of GD by hydrotreatment of vegetable oils have been observed when using metals supported in zeolites, but also in carbon, although they deteriorate selectivity (Sinha et al., 2016). This very important because if an acid substance, such as formic acid, is employed as H₂ donor, the medium is likely to have a pH less than 3.0 that will destroy the structure of the zeolite and the alumina. For this reason, activated C is recommended as support.

Few works have used the same catalyst for the generation of hydrogen and the deoxygenation of biomass. Hwang et al. (2016) studied the effect of the addition of a 30 % solution of formic acid as a source of hydrogen for the production of GD from crude jatropha oil by catalytic deoxygenation on Pd/C in a batch reactor. Using formic acid with this catalyst, a 99 % conversion of the oil and a 97 % selectivity towards hydrocarbons were found. In addition, there was greater resistance to the initial deactivation suffered by the catalyst (Hwang et al., 2016). Another research that uses a catalyst composed of palladium nanoparticles supported on titanium oxide and mesoporous carbon modified with nitrogen Pd/TiO₂@NC shows that this support provides excellent stability for the hydrogenation of vanillin using formic acid as a source of hydrogen (Wang, et al., 2014). In both studies, Pd/C was used for hydroprocessing of biomass in situ.

4. Conclusions

Using the Macbeth method, the noble metal family was selected, and within this family, the Pd/C catalyst may be the most promising for the production of Green Diesel by hydrotreatment in situ from triglycerides. Due to the severe process conditions (350–450 °C and 5–15 MPa), and the high cost of the noble metals that are normally used, it is imperative to develop new catalysts that improve the conversion and reactive system performance and decrease the thermal and pressure requirements of H₂ in the process. Such catalysts can be mineral residues (ashes) of thermal-catalytic processes, which have a high content of metal oxides.

References


