New Three-phase recirculation reactor for catalytic hydrogenation of vegetable oils

D. F. Saraiva, F. G. Freire, R. Carvalho

Abstract

A three-phase recirculation reactor was developed for the partial hydrogenation of vegetable oil using conventional nickel catalyst. The objective of this reactor is to reduce the process complexity and cost of an industrial scaled hydrogenation facility.

The most important advantages of this reactor over conventional three-phase reactors are the total hydrogen consumption with no need of recirculation and repressurisation; absence of mechanical agitation and no need for catalyst separation. In addition, sampling and control throughout run time are easier to achieve.

The laboratory scale reactor was designed and tested with the hydrogenation of soybean oil at pressures between 0.13 barg and 4.91 barg and in a temperature range of 100°C to 127°C with the purpose of knowing the influence of operating variables on it’s performance. Fatty acids concentration profiles during the runs were accessed with gas chromatography and a kinetic model was created based on mass balance differential equations.

Results show that higher temperatures, pressures and recirculation flow reduce serial hydrogenation selectivity, solid content and external diffusion limitations regarding the oil. It was also concluded that specific activity has an inverse relation with the catalytic bed height due to the catalyst efficiency reduction when working with multiple layers.

Internal diffusion limitations (IDL) have a direct relation with temperature and an inverse relation with hydrogen pressure. The Thiele modulus was determined to be within a range of 0.88 to 4.23 for the different species. The reactor works in the transition zone where there are small IDL regarding hydrogen and triglycerides.

Keywords: Three-phase Catalytic Reactor, Modelling, Hydrogenation, Soybean Oil, Nickel Catalyst, Thiele Modulus.

1. Introduction

Nowadays many important catalytic processes take place in three-phase reactors and, over the last decades, there has been a growing interest for multiphase catalytic reactors, whether is in the improvement of old technologies or the research of new ones.

Three-phase reactors are gas-liquid-solid contacting devices used in many diverse catalytic processes in the chemical industry such as hydrogenation, Fischer-Tropsch process, hydrotreatings and pharmaceutical intermediaries [Shigeo Nishimura, 2001].
The type of reactor used for these reactions is critical to the cost factors of the process itself, as each type of reactor presents advantages and disadvantages that might be best suited for each particular process [Paul Nels Rylander, 1985; E. Bruce Nauman, 2008]. The most used technologies are continuous slurry (CSTR), batch slurry (BSTR), trickle-bed (TBR) and tubular reactors although the most commonly used are the CSTR and BSTR [E. Bruce Nauman, 2008] with variations in the agitation, heat transfer and catalyst separation process. [USA Department of Energy, 2001; Vivek V. Ranade et al., 2011] Nevertheless a well-designed industrial reactor must always have good gas dispersion and, a high retention time and a good mass transfer between different phases. Heat transfer is also essential in order to maintain a homogeneous temperature and isothermal conditions. [A. Ramachandra et al., 1983]

Slurry systems used in heterogeneous hydrogenation operate with solid catalysts in powder form. The catalyst is mixed with the reactants by means of mechanical agitation and chaotic mixing [Thorsten Boger, et al.] hearing a perfect agitation state that together with the catalyst’s small particle size minimizes the external diffusional limitations (EDL) that can be the main limiting factor in non agitated technologies like trickle-bed or tubular reactors. The agitation also improves significantly the heat transfer. [A. Ramachandra et al., 1983]

Although it’s important to have in mind that slurry reactors have well known problems [Kapteijn et al.]: Catalyst handling as loading powder catalysts in large scale reactors requires additional safety and environmental measures; Catalyst separation which increases the overall process cost and requires once again supplementary environmental precautions and operating at high pressures [Vivek V. Ranade et al., 2011] due to potential gaslet failure, usually occurring in the agitation system. [E. Bruce Nauman, 2008]

A possible solution is the use of trickle-bed reactors (TBR) mostly for their operating simplicity and unique advantages for large volume processing. TBR consists of a fixed bed of solid catalyst particles contacted by a concurrent downward gas-liquid flow carrying both reactants and products. These reactors are used widely in the petrochemical sector for various hydrotreatments such as hydrodesulfurization, hydrocracking, hydorefining, hydrometalization, hydrogenation and others, with processing capacity of billions of metric tons [Muthanna H. et al. 1997] [McManus et al., 1993] Yet, the shortcomings of TBRs are the impracticality for reactions with rapidly deactivating catalysts and the possibility for liquid maldistribution, which may give rise to hotspots, reactor runaway and reaction selectivity and velocity changes. Overall performance of these reactors depends on several matters that influence hydrodynamics such as fluid phase mixing, interphase and intraparticle heat and mass transfer and reaction kinetics. [Vivek V. Ranade et al., 2011] Retention time and gas phase recovery and recirculation are matters that also influence the economical impact of TBRs.
The reactor presented in this article combines TBR technology with other reactor technologies, as loop reactors, with the purpose of solving several disadvantages of other three-phase reactors. The performance of the reactor was assessed in a laboratory scale set-up with soybean oil hydrogenation. Several operating parameters were tested.

### 1.1. Partial Vegetable Oil Hydrogenation

Partial hydrogenation of vegetable oils is a well-known process, with great importance in the food industry and more recently in the fuel industry. It aims to modify the vegetable oil properties such as oxidative and thermal stability and, in some cases, to convert liquid oils to the semi-solid form. [Maria B. Fernández et al., 2005]

The reaction is carried out in three-phase reactors, under specific conditions where only unsaturated bonds of triglycerides (TAG), the almost exclusive compounds of vegetable oils, are hydrogenated. Typically the catalysts used are nickel or noble metals supported in silica and under soft operating conditions of pressure (0.1 MPa to 0.7MPa) and temperature (100 ºC to 200ºC) [Quido Smejkal et. al., 2009; Yogesh G. Waghmare et. al. 2010] that can vary depending on the specific application.

Simultaneously to double bond saturation, hydrogenation of polyunsaturated oils also causes geometrical and positional isomerisation of the remaining double bonds, resulting in an increase of the trans fatty acid (TFA) content and hardening of fat [Maria B. Fernández et. al., 2005].

The TFA have negative health implications and moreover a slight negative impact for fuel applications. TFA increase the oil melting point weakening the cold flow properties of the oil or biodiesel produced from hydrogenated oil. The melting points of geometrical isomers cis and trans of fatty acid are compared in Table 1.

#### Table 1

<table>
<thead>
<tr>
<th>FAME common name</th>
<th>Geometrical Isomer</th>
<th>Chemical Formula</th>
<th>IUPAC name</th>
<th>Melting Point (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid</td>
<td>cis</td>
<td>C18H32O2</td>
<td>(9Z)-octadec-9-enoic acid</td>
<td>13.4</td>
</tr>
<tr>
<td>Elaidic acid</td>
<td>trans</td>
<td>C18H32O2</td>
<td>(9E)-octadec-9-enoic acid</td>
<td>12.4</td>
</tr>
<tr>
<td>Vaccenic acid</td>
<td>trans</td>
<td>C18H32O2</td>
<td>(11Z)-octadec-11-enoic acid</td>
<td>10.9</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>cis</td>
<td>C18H32O2</td>
<td>(9Z,12Z)-octadec-9,12-dienoic acid</td>
<td>8.1</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>trans</td>
<td>C18H32O2</td>
<td>(9Z,12Z)-octadec-9,12-dienoic acid</td>
<td>8.1</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>cis</td>
<td>C18H32O2</td>
<td>(9Z,12Z,15Z)-octadec-9,12,15-trienoic acid</td>
<td>16.3</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>trans</td>
<td>C18H32O2</td>
<td>(9Z,12Z,15Z)-octadec-9,12,15-trienoic acid</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Previous studies indicate that higher hydrogen pressure lowers the rate of TFA formation although, since the concentration of hydrogen at the catalyst surface is higher it will promote the formation of saturates by serial reactions [Beers, A. 2008] if hydrogen concentration was limited at lower pressures.

There are also studies of the effects of large intraparticle concentration gradients. W. A. Cordova et. al. and J. W. E. Coenen shown that both the serial reaction pathway selectivity and the stereoselectivity increase when the reaction is pore diffusion-limited with respect to triglycerides [W. A. Cordova et. al. 1975;
since under these conditions the partially hydrogenating triglycerides diffuse slower from the pores enabling them to react further [Yogesh G. Waghmare 2010].

In this case study the performance of the reactor was tested with soybean oil hydrogenation. The objective was to partially hydrogenate the soybean oil with low serial pathway selectivity and low stereoselectivity avoiding fully saturated acids and solid formation.

**Nomenclature**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>TPRR</td>
<td>Three-Phase Recirculation Reactor</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty acid methyl ester</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph / Gas Chromatography</td>
</tr>
<tr>
<td>IV</td>
<td>Iodine Value</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>P</td>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>Q_o</td>
<td>Oil recirculation flow (L/s)</td>
</tr>
<tr>
<td>W_cat</td>
<td>Catalyst mass (g)</td>
</tr>
<tr>
<td>Q_H2</td>
<td>Hydrogen flow</td>
</tr>
<tr>
<td>V_o</td>
<td>Oil volume</td>
</tr>
<tr>
<td>dt</td>
<td>Time increment</td>
</tr>
<tr>
<td>C_i</td>
<td>Inlet concentration of reagent i (mol/L)</td>
</tr>
<tr>
<td>C_iw</td>
<td>Concentration of reagent i in the catalytic bed (mol/L)</td>
</tr>
<tr>
<td>r_iw</td>
<td>Rate of consumption of specie i at concentration C_iw (mol/g_cat·s)</td>
</tr>
<tr>
<td>k</td>
<td>Kinetic constant (min⁻¹)</td>
</tr>
<tr>
<td>E_a</td>
<td>Activation energy</td>
</tr>
<tr>
<td>m</td>
<td></td>
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<tr>
<td>n</td>
<td></td>
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**Greek Letters**

**Subscripts**

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
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<tbody>
<tr>
<td>cat</td>
<td>Related to Catalyst</td>
</tr>
<tr>
<td>3</td>
<td>Related to C18:3</td>
</tr>
<tr>
<td>2</td>
<td>Related to C18:2</td>
</tr>
<tr>
<td>1</td>
<td>Related to C18:1</td>
</tr>
</tbody>
</table>
2. Experimental

2.1. Experimental set-up description

A Glass Reactor with the capacity of 1 Litre was designed and integrated in a loop system as shown in Fig. 1. The reactor had four ground glass joints sealed with grease and metallic clamps in the top. The joints allow inlet of liquid phase (soybean oil) and gas (hydrogen and nitrogen) through ¼ inch stainless steel tubing sealed with silicone sealants. Also the pressure sensor and temperature probe were inserted through the top of the reactor. The head was attached to the body with a metallic collar and sealed with a silicone O-ring. The reactor had an exit on the lateral wall 6 mm above the bottom to allow the oil to exit to the heat exchanger (HE). Heating and isothermal conditions were guaranteed by an electrical heating mantle with 300 W heating power, that surrounded the reactor. A hotplate heated the bottom of the reactor, containing the oil.

A steel basket was also created and suspended inside to hold the catalyst (Catalytic bed).

The oil was re-circulated in a closed loop when operating in batch conditions. It was admitted through the top of the reactor with an atomizer that ensures liquid atomization, small droplets and an optimal and homogeneous distribution over the Catalytic bed.

A hydraulic diaphragm pump recirculated the oil with a flow comprehended between 200 and 370 mL/minute. The pump could operate at a maximum temperature of 60°C thus the inlet flow had to be previously cooled down by a coil heat exchanger that worked with tap water. Before entering the reactor the oil was heated to the reaction temperature with an electric heat exchanger integrated in the tubing with 480 W of heating power and a preheating coil around the reactor external wall to optimise heating power.
The hydrogen (Alphagaz 2, 99.9999% - Airliquide) is admitted to the reactor separately and in co-current with the oil, as shown in Figure 1, and it was all consumed in the reaction. The system was capable of operating at a maximum pressure 5 barg and up to 130 °C.

**The catalyst** used in the experiments was a commercial nickel catalyst with 21% mass supported in alumina oxide. The catalyst was used in the form of trilobite extrudes with the nominal size of 1.2 mm, porosity of 0.33 and bulk density of 770 kg/m$^3$.

**The oil** used is neutralised soybean oil and its fatty acid methyl ester (FAME) composition is shown in table 2.

### Table 2

<table>
<thead>
<tr>
<th>FAME common name</th>
<th>Nomenclature</th>
<th>% (m/m)</th>
<th>% std dev (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic Acid</td>
<td>C16:0</td>
<td>11.51</td>
<td>1.05</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>C18:0</td>
<td>4.96</td>
<td>1.24</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>C18:1</td>
<td>24.65</td>
<td>3.16</td>
</tr>
<tr>
<td>Linoleic Acid</td>
<td>C18:2</td>
<td>50.34</td>
<td>0.88</td>
</tr>
<tr>
<td>Linolenic Acid</td>
<td>C18:3</td>
<td>6.71</td>
<td>1.17</td>
</tr>
</tbody>
</table>

It is important to note that a stainless steel net with 1mm mesh coated with glass fibre fabric with aluminium foil was used around the reactor as a safety measure preventing any potential glass shards projection that could cause health risk the operator in case of glass shattering.

### 2.2. Analysis

The experimental apparatus was equipped with a digital pressure sensor that allowed to measure hydrogen pressure in the vase to the mbar; A needle barometer to measure oil pressure before the atomizer; An internal PT100 thermometer situated above the catalytic bed and an external PT100 thermometer to measure oil temperature at the pump.

Oil flow was calibrated for the specific system (piping and diaphragm pump) in function of hydrogen pressure in the vase, diaphragm inlet % and oil temperature at the pump.

Catalyst loading was weighed in an analytical balance.

Hydrogen flow was measured with a mass flow controller (MFC) calibrated for hydrogen at PTN conditions (0ºC, 1 atm) in L/min

Data acquisition and control were carried out in LabVIEW™ software.

Experimental samples from the reactor were diluted (1:10 v/v) in n-heptane puris (≥99%) and partially transesterified in a test tube with 0.1Molar KOH in Methanol (99.9%). The resulting FAMEs were analysed using a gas chromatograph (GC) (SRI 8610C) equipped with a SP-2380 (Supelco) capillary GC column (60m x 0.25mm x 0.2µm). Chromatograms where analysed to determine fatty acids’ composition during experiment time. Positional isomers were lumped together and geometrical isomers were identified although, to simplify the kinetic modelling these isomers were also grouped.
The overall degree of the oil unsaturation was measured in terms of Iodine Value (IV), calculated indirectly using GC data and FAMEs contribution factors (Table 3) using Eq. 1. The contribution is a function of the FAMEs mass and number of double bonds that also allowed determining FAMEs molar concentration using Eq. 2. The IVs of the initial and final oil were confirmed with titration using IUPAC method II.D.7.

Table 3
FAMEs contribution to IV.

<table>
<thead>
<tr>
<th>FAME</th>
<th>IV Contribution Factor (CF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18:1</td>
<td>0.362</td>
</tr>
<tr>
<td>C18:2</td>
<td>1.732</td>
</tr>
<tr>
<td>C18:3</td>
<td>2.616</td>
</tr>
</tbody>
</table>

\[ IV = CF \times \% GC Area \]  

\[ [FAME] = \frac{CF \times \% GC Area \rho_{cat} \cdot 10}{w_t \cdot i_s} \]  

2.3. Mass Conservation equation

For purposes of interpretation regarding mass balance, the reactor was divided into two sections: The first, is the Catalytical Bed:

Considering the low volume of inlet/outlet connection (\( V_L, L \)) and flow rate (\( Q_L, L/s \)) it is said that for each infinitesimal differential of time (\( dt \)) the inlet concentration (\( C \)) is equal to the concentration in the reactor bottom that is well mixed.

Also, if the conversion in the Catalytic Bed is very low it can be considered that all catalyst is exposed to the same concentration of reagent, ensuring the bed is in homogeneous conditions and therefore concentration gradients are not taken into account.

In this case the concentration difference between the top of the catalyst bed and the bottom part of the bed can be written as:

\[ Q_L \cdot (C_{iw} - C_i) - r_{iw} \cdot W_{cat} = 0 \]  

Where:
- \( Q_L \) – Oil Volumetric flow (\( L/s \))
- \( C_{iw} \) – Concentration of reagent i in catalyst and outlet bed
- \( C_i \) – Concentration in the inlet of the Catalytic Bed
- \( W_{cat} \) – Catalyst mass (g)
- \( r_{iw} \) – rate of consumption of specie i (mol.g\(^{-1}\)s\(^{-1}\)) at concentration \( C_{iw} \)
The second part of the reactor is, as previously mentioned, the **Bottom Volume**:

The flow of concentration $C_{iw}$ will fall to the bottom of the reactor with $V_L$ volume and concentration $C_i$. The concentration variation on that volume can be deduced by:

$$Q_L \left( C_{iw} - C_i \right) - \frac{dC_i}{dt} V_L = 0 \tag{4}$$

Notice that there is no catalyst in the bottom therefore the reaction only takes place in the **Catalytical bed**.

Now is possible to describe the Three-Phase Recirculation Reactor (TPRR) through Eq. 3 and 4:

Replacing $Q_L \left( C_{iw} - C_i \right)$ of Eq. 4 in 3 it solved as:

$$\frac{dC_i}{dt} V_L = r_{iw} W_{cat} \tag{5}$$

As the **Catalytical Bed** has a low conversion ($C_i \approx C_{iw}$), the balance can be written as:

$$\frac{dC_i}{dt} V_L = r_i W_{cat} \tag{6}$$

Eq. 6 shows that this reactor can be seen as a batch reactor of volume $V_L$ with a catalyst with mass $W_{cat}$. Evidently this is correct if and only if $V_d/Q_L$ is low and there is optimal oil dispersion over the catalyst.

### 3. Results and Discussion

#### 3.1. Catalytic Activity.

The TPRR was used in batch mode and several runs were carried out. The main operating variables were varied. The **Catalytic Bed** temperature (T) was varied between $99.88^\circ C$ and $126.23^\circ C$; hydrogen pressure (P) was varied from 0.13 barg up to 4.91 barg; $Q_L$ between 258.45 ml/min and 379.8 ml/min and $W_{cat}$ between 8.003 g and 35.044 g.

The instantaneous hydrogenation activity of the catalytic reaction was accessed by the flow rate of $H_2$ ($Q_{H_2}$) measured with the MFC. This measured activity must be related to the total rate of hydrogenation process in the reactor:

$$Q_{H_2} = V_{H_2} \sum_{i=1}^{n} r_i W_{cat} \tag{7}$$

Where:
- $V_{H2}$ is the molar volume of H$_2$ at PTN (L/mol);
- $n$ is the number of hydrogenation reactions;

Assuming first order to the reagent and that the H$_2$ pressure is constant at all time, $r_i$ can be expressed as

$$r_i = k_i C_i W_{cat}$$  \hspace{1cm} (8)

If this thought process is extended to all hydrogenation reactions, it will be obtained an apparent activity ($\alpha$) measured as:

$$\alpha = \frac{Q_{H2} W_{cat}}{V_{H2} W_{cat}} \left\lbrack \text{mol/} \text{g catalyst} \cdot \text{min} \right\rbrack$$  \hspace{1cm} (9)

Also catalytic activity was also determined and verified using IV definition [Yogesh G. Waghmare 2010] that leads to Eq. 10.

$$\alpha = \frac{\Delta W_{oil} V_{oil}}{\Delta t \cdot 100 \cdot W_{cat} \cdot \text{wt} \cdot f_2} \left\lbrack \text{mol/} \text{g catalyst} \cdot \text{min} \right\rbrack$$  \hspace{1cm} (10)

The experimental conditions and activity results are summarised in Table 4.

| Run number | T (ºC) | T std dev (ºC) | P (barg) | P std dev (barg) | Q$_i$ (ml/min) | Q$_i$ std dev (ml/min) | t (min) | $W_{cat}$ (g) | Initial IV | Final IV | $\alpha$ @180min (mol H$_2$/(g cat) min)$^{-1}$ x10$^5$
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1</td>
<td>101.92</td>
<td>5.17</td>
<td>1.17</td>
<td>0.02</td>
<td>379.89</td>
<td>7.89</td>
<td>400</td>
<td>8.0030</td>
<td>129.68</td>
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<td>3.51</td>
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<tr>
<td>2</td>
<td>103.86</td>
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<td>1.04</td>
<td>420</td>
<td>12.6131</td>
<td>128.7</td>
<td>109.9</td>
<td>3.69</td>
</tr>
<tr>
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<td>100.88</td>
<td>4.14</td>
<td>1.07</td>
<td>0.01</td>
<td>364.89</td>
<td>5.56</td>
<td>420</td>
<td>35.0443</td>
<td>126.31</td>
<td>97.98</td>
<td>2.23</td>
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<td>4</td>
<td>106.54</td>
<td>1.30</td>
<td>1.11</td>
<td>0.04</td>
<td>284.65</td>
<td>1.34</td>
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<td>34.3430</td>
<td>123.7</td>
<td>102.21</td>
<td>2.61</td>
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<tr>
<td>5</td>
<td>126.23</td>
<td>3.46</td>
<td>1.01</td>
<td>0.01</td>
<td>326.41</td>
<td>4.11</td>
<td>180</td>
<td>34.3430</td>
<td>122.82</td>
<td>95.07</td>
<td>4.69</td>
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<tr>
<td>6</td>
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<td>0.13</td>
<td>0.01</td>
<td>258.45</td>
<td>3.68</td>
<td>300</td>
<td>34.1568</td>
<td>126.39</td>
<td>106.47</td>
<td>2.49</td>
</tr>
<tr>
<td>7</td>
<td>107.75</td>
<td>2.39</td>
<td>0.62</td>
<td>0.01</td>
<td>303.35</td>
<td>2.64</td>
<td>180</td>
<td>34.1568</td>
<td>125.47</td>
<td>106.99</td>
<td>3.14</td>
</tr>
<tr>
<td>8</td>
<td>111.35</td>
<td>0.85</td>
<td>4.91</td>
<td>0.23</td>
<td>342.53</td>
<td>0.87</td>
<td>180</td>
<td>35.0165</td>
<td>126.53</td>
<td>106.99</td>
<td>3.35</td>
</tr>
</tbody>
</table>

The results show that, under the same operating conditions of T, P and Q$_i$, the specific activity is reduced when $W_{cat}$ is increased from 12 g to 35 g. Since the catalytic basket is the same between runs, it is expected that, when added more catalyst, the catalytic bed will be higher thus adding more layers. Each catalyst layer has approximately 12 grams.

When working with a monolayer of catalyst the superficial area is fully utilized, all the particles are totally wet and the oil concentration and composition are homogeneous in the catalyst surface.

When more layers are added preferential flow may occur as well as partial wetting and oil stagnation leading to heterogeneous distribution of oil
concentration and composition and more importantly lower hydrogen concentrations in-between catalyst layers.

These facts explain why the activity was smaller when working with three layers of catalyst.

When comparing Runs 4, 6 and 7, where there was a Q_L variation it can be confirmed that there is an activity increase when the Q_L flow increases, that again for the same reasons it will increase the renewal rate of the oil layer in the catalyst surface therefore it will increase the hydrogen concentration in the catalyst surface (reducing EDL).

When increasing hydrogen pressure in run 8 a small increase of activity was verified. This might be a combined effect of both oil recirculation flow increase and hydrogen pressure that contribute for a higher hydrogen concentration in the catalyst surface (lower EDL and IDL).

3.2. Kinetic Constants and Selectivity

To determine kinetic constants (k) of the reaction a mechanism was firstly defined.

The hydrogenation of vegetable oil can be complex as there are many species interacting. For this study a simplified hydrogenation pathway was used:

\[
C_{18:3} \xrightarrow{k_3} C_{18:2} \xrightarrow{k_2} C_{18:1} \xrightarrow{k_1} C_{18:0}
\]

(11)

This hydrogenation mechanism is used by many authors [Yogesh G. Waghmare 2010, Jan W. Veldsink] it simplifies data analysis nonetheless it doesn’t have into account isomerisation.

Information concerning geometrical isomers of the FAMEs (cis and trans) was also gathered and it wasn’t disregarded, although for the kinetic study all the isomers were lumped together.

Four to six samples were taken during each run and analysed according to section 2.2 procedure. FAMEs profiles throughout time allowed determining k values using the Method of Initial Rates (MIR), suitable for low conversions. MIR consists in fitting an n° order polynomial function to the experimental points (n corresponding to the reaction order). In this case the best fit was a linear fit confirming that the reaction is a first order reaction.

Given the reaction mechanism in Eq. 11, ks were determined using the following equations:

\[
\frac{dC_{18:3}}{dt} = -k_3 \cdot C_{18:3}
\]

(12)

\[
\frac{dC_{18:2}}{dt} = k_3 \cdot C_{18:3} - k_2 \cdot C_{18:2}
\]

(13)

\[
\frac{dC_{18:1}}{dt} = k_2 \cdot C_{18:2} - k_1 \cdot C_{18:1}
\]

(14)
Eq. 15 wasn’t used for calculations, as it is dependent. The kinetic constants were determined for an average temperature of 111.9°C ±0.2°C and are shown in Table 5.

Selectivity is a term used to describe the relative rates of two or more competing reactions on a catalyst. In the particular case of this reaction the competition is between different reactants undergoing hydrogenation simultaneously.

It’s usual to call the hydrogenation selective if it’s predominant over less saturated than over more saturated triglycerides.

\[ S_{32} = \frac{k_3}{k_2}; S_{21} = \frac{k_2}{k_1} \]  

The determined average value for \( S_{32} \) and \( S_{21} \) were 1.50±0.14 and 1.92±0.21 respectively. When comparing these values with typical values obtained in typical stirred tank reactors [Yogesh e mais] one can see that \( S_{32} \) is much lower, being the typical value of 8 to 12 [Yogesh e mais].

This is due to the larger particle size and the lower renewal rate of the film of TAGs in the surface of the catalyst. Both reasons lead to serial hydrogenation and reduction of \( S_{21} \).

### 3.3. Kinetic Modeling

Kinetic modelling is a tool that allows obtaining kinetic parameters by using mass balance equations and kinetic equations to describe the system and reaction respectively. The ordinary differential equations (ODE) were solved using Euler method in Microsoft Excel™. Kinetic parameters as the kinetic constants and activation energies (\( E_a \)) were obtained. Also, to confirm the relation order of kinetics with \( Q, W \) and \( P \) the Eq. 5 was modified and combined with Eq. 12 to 15. The following ODEs were obtained:

\[
\frac{dC_{C18:0}}{dt} = k_1 C_{C18:1} \tag{15}
\]

\[
\frac{dC_{C18:1}}{dt} = \frac{(k_3 C_{C18:3} - k_2 C_{C18:2}) P_{\text{cat}}^m}{V_L^n} \tag{16}
\]

\[
\frac{dC_{C18:2}}{dt} = \frac{(k_2 C_{C18:3} - k_1 C_{C18:1}) P_{\text{cat}}^m}{V_L^n} \tag{17}
\]

\[
\frac{dC_{C18:0}}{dt} = \frac{k_2 C_{C18:2} P_{\text{cat}}^m}{V_L^n} \tag{18}
\]
where \( h \) is the partial order of hydrogen pressure, \( m \) the partial order of catalyst mass and \( n \) the partial order for volume.

The model was solved for all the runs and the \( k \) and \( E_a \) values are in Table 5.

### Table 5

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k \times 10^3 ) (min(^{-1}))</th>
<th>( k \text{ std dev} \times 10^3 ) (min(^{-1}))</th>
<th>( E_a ) (kJ)</th>
<th>( E_a \text{ std dev} ) (kJ)</th>
<th>( k \times 10^3 ) (min(^{-1}))</th>
<th>( E_a ) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.50</td>
<td>0.62</td>
<td>30.16</td>
<td>3.82</td>
<td>1.91</td>
<td>43.22</td>
</tr>
<tr>
<td>2</td>
<td>1.71</td>
<td>0.64</td>
<td>42.77</td>
<td>5.53</td>
<td>1.56</td>
<td>40.45</td>
</tr>
<tr>
<td>3</td>
<td>0.98</td>
<td>0.25</td>
<td>22.68</td>
<td>5.31</td>
<td>0.59</td>
<td>19.26</td>
</tr>
</tbody>
</table>

The values obtained for the kinetic constants and \( E_a \) through the kinetic modelling are in agreement with the values obtained through MIR with exception to \( k_1 \) and \( E_{a3} \).

Selectivities \( S_{22} \) and \( S_{21} \) are 1.3 and 2.64 respectively. \( S_{21} \) is higher in consequence of a lower value of \( k_1 \).

It is very important to notice that the model doesn’t take into account diffusion, thus it considers that there are neither concentration gradients nor diffusional limitations. Furthermore the model doesn’t include serial hydrogenation due to poor oil renewal on the catalyst surface. These facts explain why \( k_1 \) is higher when obtained directly through experimental data. In order to confirm this hypothesis the concentration profiles were studied further in this section.

The partial orders of \( P, W \) and \( Q_L \) implemented in the model (Eq. 15 to 18) were as expected. The kinetic rate is independent of the Pressure, as the estimated order was 0. The model estimated the orders \( n \) and \( m \) to be 1.06 and 0.96, being very close to the unit thus coherent with Eq. 5.

#### 3.3.1. Fatty Acids concentration profiles

The experimental points were represented against the model fit for the four fatty acid species in the studied mechanism. In addition the IV variation throughout run time was represented against model indirect estimation using fatty acid concentrations.

In each set of images one single operational variable (\( T, W_{cat}, Q_L, P \)) was varied at a time, to analyse the influence of each variable.

- **Temperature variation**

When varying temperature, the model interprets the concentration evolution correctly for all species, according to Arrhenius law. The average relative error of the model for all the species at 12.0% for 100°C, 6.2% for 111°C and and 6.1% for 126°C.
Fig. 2 - Profiles of fatty acids concentration vs. time at 3 different temperatures (white for 126°C; black for 100°C; grey for 111°C) and the respective model fit (--- - - - - -). The fatty acids are C18:3 (○,◆,□), C18:2 (□,●,●), C18:1 (△,▲,▲) and C18:0 (■,■,■).

- Catalyst mass variation

There is a direct relation with the increase of catalyst weight and reaction rate, as an increment of catalyst mass translates in more active centers, however the experimental increment ratio was not 1:1. The partial order to the catalyst mass predicted by the model was of 0.96 and the experimental results show that when stacking layers of catalyst the efficiency will be reduced as explained in section 3.1. The analysis of the fatty acid profiles only supports the results obtained with the catalyst activity. The relative errors of the model for the 8 g, 13 g and 34 g runs are 4.9%, 6.7% and 4.3% respectively, showing that the model fit is good across the range of catalyst mass tested.
Regarding the variation of oil recirculation flow \((Q_L)\) it can be seen a small discrepancy between the experimental results and the model. According to the model all the reaction rates are independent of \(Q_L\) and therefore the selectivity should not vary but, in reality, it can be seen that when the flow is increased selectivity \(S_{21}\) is changed. In other words, \(k_1\) has an inverse relation with \(Q_L\).

If the hypothesis is correct it is expected the error of the model to be higher for C18:0 and C18:1 at a higher \(Q_L\). The relative errors of the model for 18:0 at 253, 284 and 364 ml/min of \(Q_L\) are 7.2%, 10.1% and 21.0% respectively. Looking at the errors of the model for 18:1 they are 3.4%, 3.6% and 6.3%. These results confirm the hypothesis.

Selectivity change with \(Q_L\) is the first indicator that the reactor is working with diffusional limitations. This hypothesis will be confirmed with the determination of the Thiele modulus further in this article.

**Oil recirculation flow variation**

![Fig. 3 - Profiles of fatty acids concentration vs. time at 3 different Catalyst mass (white for 13 g; black for 34 g; gray for 8 g) and the respective model fit (---; ---; ---). The fatty acids are are C18:3 (●●●●●), C18:2 (○○○○○), C18:1 (△△△△△) and C18:0 (□□□□□).](image)
Fig. 4 - Profiles of fatty acids concentration vs. time at 3 different Recirculation flows (white for 284 ml/min; black for 364 ml/min; grey for 253 ml/min) and the respective model fit (---). The fatty acids are C18:3 (○, ●), C18:2 (○, ●); C18:1 (△, ▲) and C18:0 (□, ▼).

**Hydrogen Pressure variation**

The higher the hydrogen pressure is, the higher the concentration of hydrogen at the catalyst surface will be, since the gas diffusivity increases with pressure as well as the solubility. Given this, if there are diffusional limitations to the hydrogen there should be a significant increase of activity at higher pressures, however it was seen that when increasing pressure to 4.91 barg only a slight change of activity occurred. In this case, either diffusional limitations of hydrogen were diminished and the diffusing rate of the fatty acids is ruling the reaction rate or the reactor is simply working free of diffusional limitations, but it is very likely that the former hypothesis is incorrect.

At this point, seeing that there is no significant variation of the reaction rates when varying the pressure, can only mean that there was no significant variation in the internal or external diffusional limitations of the various species as the reaction rate is independent of the pressure.
3.4. Trans Content

The trans isomer content in the initial soybean oil is non-existent. As the hydrogenation progresses occurs trans fatty acid (TFA) formation. The TFA content was determined over time using GC. Although it is known that TFA formation has an inverse relation with pressure and a direct with temperature, results show that the formation of TFA was not sensitive to the variations imposed except for catalyst mass.

The results were separated into two sets when comparing TFA. The first set corresponds to an average catalyst loading of 14.89±3.14 g and in the other set the average catalysts weigh was of 34.51±0.41 g. When increasing catalyst mass the observed hydrogenation rate increases thus reducing isomerisation and selectivity towards trans hydrogenation.
3.4.1. Iodine Value

The iodine value is a good indicator of the reaction conversion as it gives the amount of double bonds in the oil. The developed model can interpret the fatty acid evolution reasonably despite some higher relative errors in specific cases. When estimating the IV by using the fatty acid concentrations obtained by fitting the model to the results the average relative error obtained is below 3.5%.

3.5. Thiele Modulus

To evaluate the intraparticle diffusion limitations the Thiele module was determined.

The Thiele module represents the ratio of the surface reaction rate to the diffusion rate of a reactant within the pores of a catalyst. Considering a first order reaction the Thiele modulus, $\phi_T$, at steady state and isothermal conditions is described by Eq. 19.

$$\phi_T = \frac{R_s}{3} \sqrt{\frac{k_{\text{cat}}}{D_{\text{eff}}}}$$

(19)
Where \( R_s \) is the spherical radius of the catalyst particle; \( k \) is the real kinetic constant of the reaction; \( \rho_{cat} \) the catalyst density and \( D_{eff} \) the effective diffusivity.

The real kinetic constant is higher than the observed kinetic constant due to the effectiveness of the catalytic bed. Eq. 20 defines the effectiveness factor:

\[
\eta = \frac{\varepsilon_{obs}}{k} = \frac{1}{\phi_T} \left( \frac{1}{\tanh 3\phi_T} - \frac{1}{3\phi_T} \right)
\]  

(20)

Then combining Eq. 19 and Eq. 20, the real Thiele modulus can be determined using Eq. 21:

\[
\kappa_{obs} \phi_T \frac{\varepsilon}{3 D_{eff}} = \phi_T \left( \frac{1}{\tanh \phi_T} - \frac{1}{\phi_T} \right)
\]

(21)

### 3.5.1. Effective Diffusivities

The effective diffusivity is the real diffusivity of the molecules inside the catalyst pores and Eq. 22 gives:

\[
D_{eff} = \frac{\varepsilon D_i}{\tau} \quad i = \text{TAG, } H_2
\]

(22)

Where \( \varepsilon \) is the catalyst porosity, calculated using pore volume and density; \( \tau \) is the tortuosity, estimated to be 3.35 as the typical tortuosity of this type of catalyst [Kostas C. Metaxas, 2008] and \( D_i \) is the diffusivity.

The diffusivity of triglycerides was determined from [Jan W. Veldsink] based on [Yogesh] analogy of similar properties between soybean oil and cottonseed oil.

Hydrogen diffusivity in soybean oil was determined using Wilke-Chang correlation for diffusion in liquids:

\[
D^o_{AB} = \frac{7.4 \times 10^{-8}(\phi M_B)^{1/2}T}{6\pi \eta_B V_A}
\]

(23)

Being \( D^o_{AB} \) the coefficient of mutual diffusion of the solute A in very low concentrations in the solvent B, given in cm²/s. \( M_B \) is the molecular weigh of the solvent, in g/mol; \( T \) is the absolute temperature in Kelvin; \( \eta_B \) is the viscosity of the solvent B, in cP; \( V_A \) is the molar volume of the solute A at the boiling temperature, in cm³/mol, and final the \( \Phi_T \) is the association factor of the solvent B, it is non-dimensional and it is 1 for non-associated solvents [Bruce E. Poling, 2004].
In the present case, the solute is hydrogen and the solvent soybean oil. All the properties needed for the calculation were determined in Aspen Plus™. The diffusivities are resumed in Table 6.

<table>
<thead>
<tr>
<th>T (ºC)</th>
<th>P (barg)</th>
<th>$D_{H2} \times 10^9$ (m²/s)</th>
<th>$D_{TAG} \times 10^{10}$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.0</td>
<td>1.0</td>
<td>2.81</td>
<td>2.80</td>
</tr>
<tr>
<td>126.0</td>
<td>1.0</td>
<td>7.80</td>
<td>4.20</td>
</tr>
</tbody>
</table>

Knowing the diffusivities the Thiele modulus could be determined. It was determined for 108ºC and 1.1 barg and 126ºC and 1.1 barg for hydrogen and the different TAGs involved in the reactions.

<table>
<thead>
<tr>
<th>T (ºC)</th>
<th>P (barg)</th>
<th>Φ</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>1.1</td>
<td>1.37</td>
<td>0.55</td>
</tr>
<tr>
<td>126</td>
<td>1.1</td>
<td>1.04</td>
<td>0.66</td>
</tr>
<tr>
<td>108</td>
<td>1.1</td>
<td>0.96</td>
<td>0.69</td>
</tr>
<tr>
<td>126</td>
<td>1.1</td>
<td>0.80</td>
<td>0.72</td>
</tr>
<tr>
<td>108</td>
<td>1.1</td>
<td>2.82</td>
<td>0.31</td>
</tr>
<tr>
<td>126</td>
<td>1.1</td>
<td>4.23</td>
<td>0.22</td>
</tr>
<tr>
<td>111</td>
<td>4.9</td>
<td>1.24</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Commented [DS55]: Não quiz alongar esta determinação mas se for necessário está feita.
The results show that, under these ranges of temperatures and pressures, the reactor is always working in a transition zone of internal diffusional limitations since all the determined values are between 0.13 and 4.91. This results confirm the hypothesis formulated in section 3.3.1 when looking at fatty acid profiles variation vs. pressure.

Looking at TAG Thiele module it can be seen that C18:1 is the only that has an inverse relationship with temperature. When rising temperature, oil viscosity is reduced consequently improving oil flux through the catalytic bed and reducing serial hydrogenation. Though the self diffusion coefficient of oil doesn't suffer a great change between this range of temperatures the reaction rate for the formation of C18:1 does. It will be greatly reduced and that translates in a lower Thiele modulus.

When increasing temperature the Thiele modulus for hydrogen is strongly affected. It is expected to increase as the diffusivity has a direct linear relationship with temperature and in the other hand reaction rate raises exponentially with temperature. Then pressure is increased to 4.91 barg the estimated diffusivity of hydrogen is not affected although the solubility will be greater, thus the concentration at the catalyst surface will be considerably higher. Furthermore the observed reaction rate only suffered a slight increase. In this conditions the IDL should be significantly reduced. To confirm this hypothesis the Weisz-Prater module was determined.

### 3.6. Weisz-Prater Modulus

To confirm if intraparticle diffusion is rate-limiting the Weisz-Prats modulus was determined for TAGs and hydrogen based on the observed rates.

\[
\phi_{wp,i} = \frac{r_{H2,cat}(\varphi_E/\varphi)}{\text{area}_{eff} C_i}; \quad i = \text{TAG}, H_2
\]

where \(r_{H2}\) is the observed catalytic activity, or rate of hydrogen consumption in mol/g\_cat\_s and \(C_i\) is the concentration of the specie \(i\) in the surface of the catalyst.

The concentration of TAGs was determined using Eq. 2.

The concentration of hydrogen at the catalyst surface was estimated using data from [Jan W. Veldsink]. The estimated concentration was of 9.1 mol/m\(^3\) of oil and 22.8 mol/m\(^3\) of oil at 1 bar and 5 bar respectively.

<table>
<thead>
<tr>
<th>Table 8</th>
<th>Weisz-Prater modulus for the the different TAG and hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>P (barg)</td>
</tr>
<tr>
<td>C18:3</td>
<td>108</td>
</tr>
<tr>
<td>C18:2</td>
<td>108</td>
</tr>
</tbody>
</table>
The Weisz-Prater module confirms the hypothesis that, when increasing pressure the IDL for hydrogen are greatly reduced. Also it was possible to see small limitations regarding TAG as expected.

4. **Conclusions**

The stirred tank reactor is also the most widely used reactor in laboratory, but the scale-up is somewhat difficult when the geometry is changed for trickle bed or even for the same geometry and only a size increase.\(^\text{[3,5]}\) Furthermore, it is difficult to operate a laboratory continuous slurry reactor because of the need to retain the catalyst and liquid volume phase. For an easier scale-up and to eliminate the most significant disadvantages of slurry reactors previously mentioned, it is presented in this article a new kind of reactor and the respective results regarding its performance, tested with a hydrogenation reaction.

**References**


Thorsten Boger, Martijn M. P. Zieverink: Monolithic Catalysts as an Alternative to Slurry Systems

[10]