

Electronic Supplementary Information

Optimization of the Catalytic Production of Methyl Stearate by Applying the Response Surface Box-Behnken Design: An Intensified Green Option for High-Cetane Biofuel Manufacture

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S1. Experimental esterification reaction

S1.1. Equipment

Due to the size and configuration of the stator head dispersion attachment to avoid the vaporization of the remaining methanol, an airtight sleeve stopper was tight to reactor nozzle. Additionally, a semi-transparent and flexible film (Parafilm) was used to provide additional isolation.

S1.2. Catalyst removal

Upon reaction and after removing the excess of methanol, two non-miscible phases are visible with the top layer consisting of a mixture between methyl stearate and unreacted stearic acid; these two compounds have a non-polar natura as they both have a long hydrocarbon chain. The bottom layer is basically the that is produced during reaction. After removing the bottom layer, hot deionized water is added to the catalyst (sulfuric acid). It is worthwhile mentioning that the acid value (AV) measurement must be conducted upon removal of the remaining sulfuric acid to have precise measurements.

S1.3. Acid value technique

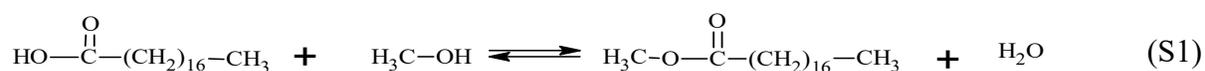
The quantification of AV of fats, oils and grasses via titration is an official method established by the American Oil Chemists' Society (AOCS);¹ it is in fact a well-accepted low-cost method to determine de AV. The titration classic method and ¹H NMR have been compared for the free fatty content determination finding similarities in results.^{2,3}

S2. High shear mixing in the esterification reaction

As mentioned in the main article, some processes involving chemical reactions have been intensified by applying high shear mixing (HSM). Hence, preliminary experiments were

conducted to verify the initial effect of HSM in the esterification reaction between stearic acid (SA) and methanol to produce methyl stearate and water (see equation S1). Regarding the methanol:SA molar ratio, the initial experiments were conducted using the stoichiometric amount to carry out the reaction; however, the reaction mixture was not homogeneous.

The low severity temperature was defined at 40 °C; at this condition, SA melts and can be easily manipulated when is in the fluid liquid. The high severity temperature was set to 60 °C to avoid methanol vaporization as its normal boiling point of is 65 °C.



A preliminary investigation of the effect of the HSM speed from 500-2000 rpm on SA conversion (see Fig. S1) was carried out at both low severity (1 min, 40°C, 0.25% cat and 7:1 methanol:SA) and high severity (12 min, 60°C, 4% cat and 13:1 methanol:SA) experimental conditions.

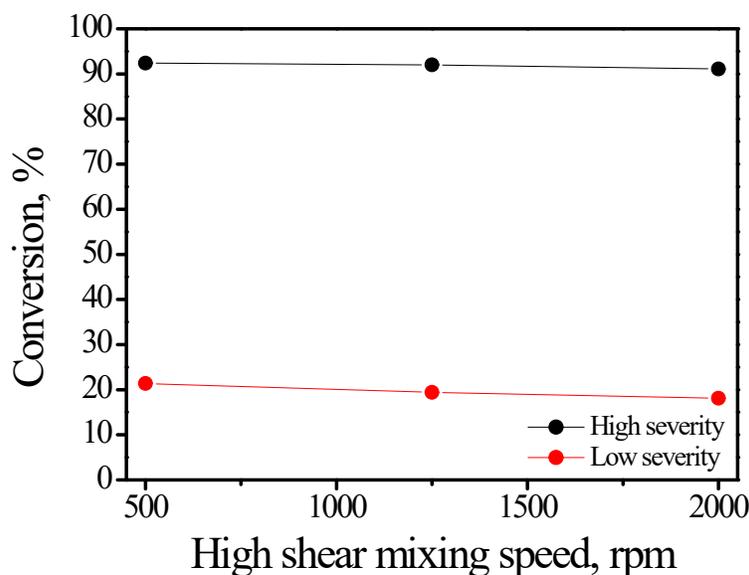


Fig. S1. Effect the mixing speed in the Esterification of SA with methanol assisted by the high shear mixing.

The information in Fig. S1 indicates that, apparently, at the two experimental severity levels (low and high), the effect of increasing the high shear speed rate was not relevant on SA conversion, an issue that can be explained in terms of diverse size-droplets produced during dispersion in the rotor–stator. In fact, a perfect mixture between liquid-liquid phases (reactants and catalyst) is generated conducting an effective mass diffusion among phases.⁴ Accordingly, a reaction time reduction is noticed, a behavior that has been previously reported.⁵ From these results, the HSM mixing speed was removed from the Box-Behnken design (BBD) to have a more manageable design of experiments, setting its value to a constant value equal to 500 rpm.

S3. Defining the Box-Behnken experimental region

Preliminary experiments were carried for delimiting the experimental operating zone for the BBD. Factors were independently analyzed at low and high experimental conditions (*vide* Table S1).

Table S1 Preliminary experiments for delimiting the BBD experimental region.

Factor and interval		Low severity conditions	High severity conditions
Methanol:SA ratio, mol/mol	7:1 – 13:1	0.25 wt% Cat, 1 min, 40 °C.	4 wt% Cat, 12 min, 60 °C.
Catalyst mass, wt%	0.25 – 4	7:1 methanol:SA, 1 min, 40 °C.	13:1 methanol:SA, 12 min, 60 °C.
Temperature, °C	40 – 60	0.25 wt% Cat, 7:1 methanol:SA, 1 min.	4 wt% Cat, 13:1 methanol:SA, 12 min.
Time, min	1 – 12	0.25 wt% Cat, 7:1 methanol:SA, 40 °C.	4 wt% Cat, 13:1 methanol:SA, 60 °C.

Primary experiments are summarized in Fig. S2, where the middle point was incorporated to visualize curvature effects. In general, curvature was evident for each factor hereafter the BBD that include a large population of experiments at the middle point of the experimental range is an adequate design of experiments to compute the linear and quadratic effects along with binary interactions.

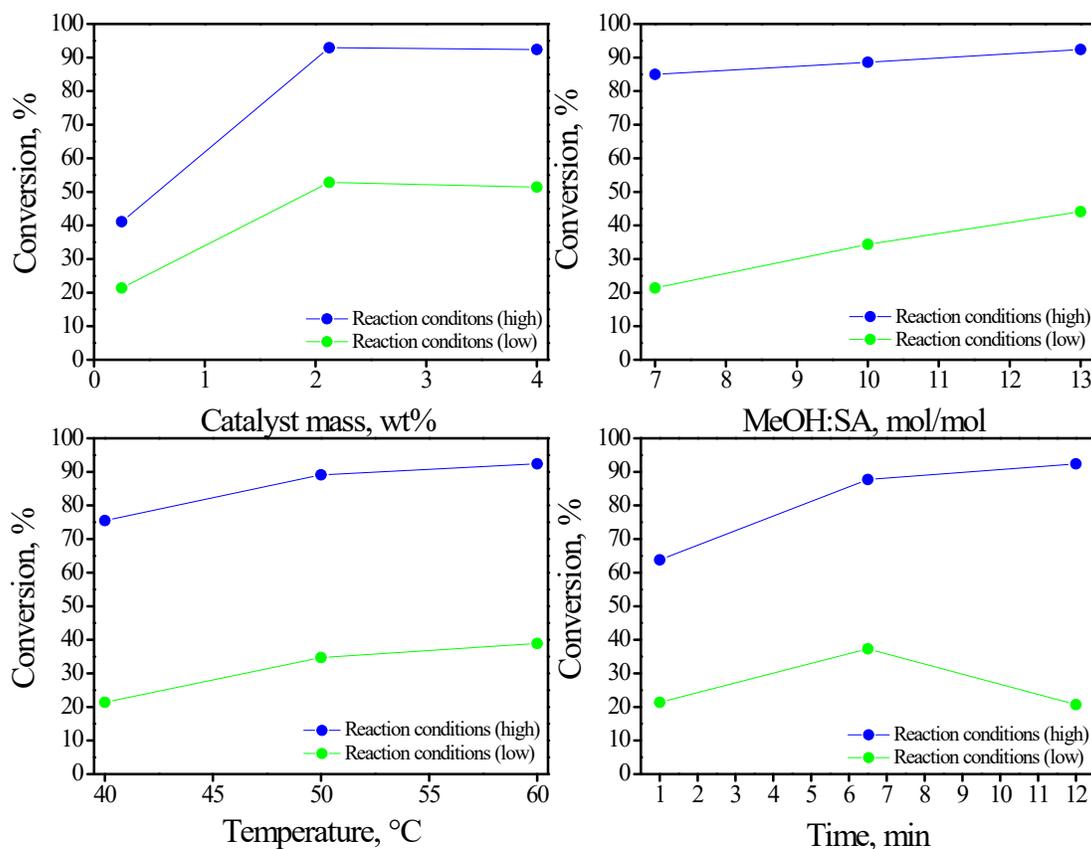


Fig. S2. Initial esterification experiments for delimiting the BBD experimental region.

S4. Box-Behnken design's complete experimental matrix

Table 1 in main document shows the specific Box-Behnken design experimental region or factors' limits. As four factors were incorporated into the BBD and some replicated experiments were added to compute the pure error, the total number of runs amounted to 27 (see Table S2); that is, 24 base runs in a semi-factorial block and 3 replicated runs at the center point. In this

table, the specific values and coding of the factors were incorporated: recall that the BBD accounts for 3 levels per factor, namely, low “-1”, middle center “0” and high “+1” levels.

Table S2 Full experimental matrix of the BBD containing the specific conditions of the four factors in each individual experiment.

Run	Methanol:SA ratio, mol/mol	Catalyst mass, wt%	Temperature, °C	Time, min
1	-1 (7.0)	-1 (0.25)	0 (50)	0 (6.5)
2	+1 (16.0)	-1 (0.25)	0 (50)	0 (6.5)
3	-1 (7.0)	+1 (4.0)	0 (50)	0 (6.5)
4	+1 (16.0)	+1 (4.0)	0 (50)	0 (6.5)
5	0 (11.5)	0 (2.125)	-1 (40)	-1 (1.0)
6	0 (11.5)	0 (2.125)	+1 (60)	-1 (1.0)
7	0 (11.5)	0 (2.125)	-1 (40)	+1 (12.0)
8	0 (11.5)	0 (2.125)	+1 (60)	+1 (12.0)
9	-1 (7.0)	0 (2.125)	0 (50)	-1 (1.0)
10	+1 (16.0)	0 (2.125)	0 (50)	-1 (1.0)
11	-1 (7.0)	0 (2.125)	0 (50)	+1 (12.0)
12	+1 (16.0)	0 (2.125)	0 (50)	+1 (12.0)
13	0 (11.5)	-1 (0.25)	-1 (40)	0 (6.5)
14	0 (11.5)	+1 (4.0)	-1 (40)	0 (6.5)
15	0 (11.5)	-1 (0.25)	+1 (60)	0 (6.5)
16	0 (11.5)	+1 (4.0)	+1 (60)	0 (6.5)
17	-1 (7.0)	0 (2.125)	-1 (40)	0 (6.5)
18	+1 (16.0)	0 (2.125)	-1 (40)	0 (6.5)
19	-1 (7.0)	0 (2.125)	+1 (60)	0 (6.5)
20	+1 (16.0)	0 (2.125)	+1 (60)	0 (6.5)
21	0 (11.5)	-1 (0.25)	0 (50)	-1 (1.0)
22	0 (11.5)	+1 (4.0)	0 (50)	-1 (1.0)
23	0 (11.5)	-1 (0.25)	0 (50)	+1 (12.0)
24	0 (11.5)	+1 (4.0)	0 (50)	+1 (12.0)
25	0 (11.5)	0 (2.125)	0 (50)	0 (6.5)
26	0 (11.5)	0 (2.125)	0 (50)	0 (6.5)
27	0 (11.5)	0 (2.125)	0 (50)	0 (6.5)

References

- 1 American Oil Chemists' Society (AOCS), <https://www.aocs.org/attain-lab-services/methods/methods/search-results?method=111545>, 2017 (accessed: September 18th 2023).
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