AIDIC
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FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Heterogeneous hydrogenation of rapeseed oil and FAME with copper supported on silica catalysts in slurry batch reactor: activity and kinetics of reaction.

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Highlights

- Cu catalysts development for catalytic hydrogenation of rapeseed oil and derivatives.
- Batch reactor for the selective hydrogenation of oils and methyl esters.
- Tests conducted in real conditions.
- Kinetic study of the reaction.

1. Introduction

As attested in other studies vegetable oils are a viable alternative to petroleum in the preparation of industrial interesting products [1][2]. However, to stabilize the degree of oxidation of oils or their derivatives (FAME) and to use them, lowering the degree of unsaturation is necessary but it is best to avoid complete saturation of the raw materials; commonly a content of around 88% of mono-unsaturate compound is considered the optimum. Of all possible configurations, the cis isomer, oleic acid (C18:1c), is preferred with respect the trans isomer. Obtain high concentration of cis-monoenes is possible with selective hydrogenation. In this work heterogeneous catalysis for hydrogenation was considered, particularly, as active phase for this reaction was chosen copper since its activity towards complete saturation is lower than other transition metals (Ni, Pt, Pd, etc.)[3]. The catalysts was tested in a hydrogenation unit developed and already tested in precedent works which will be presented at CATBIOR 2017 [4] and IBIC 2018 [5] conferences.

2. Methods

Copper based catalysts, supported on silica, are produced with two different synthetic paths: the Hydrolysis-Precipitation (HP) method [6] and Ammonia Evaporation (AE) method [7], with different Cu loading between 5÷15% w/w. The first catalyst is produced from tetraethyl orthosilicate and the second from colloidal silica. The catalysts endure the same thermal treatment at 450 °C for 4h and then it is reduced at 450 °C for 2h under 10% atmosphere of H_2 in N_2.

Each catalyst is characterized with the following techniques: XRD, Raman and FTIR for crystal phases identification, BET-BJH for surface area and pore size distribution, ICP determination of copper loading, TPR reduction temperature for studying interactions between catalysts and support. The campaign of characterization is in progress.

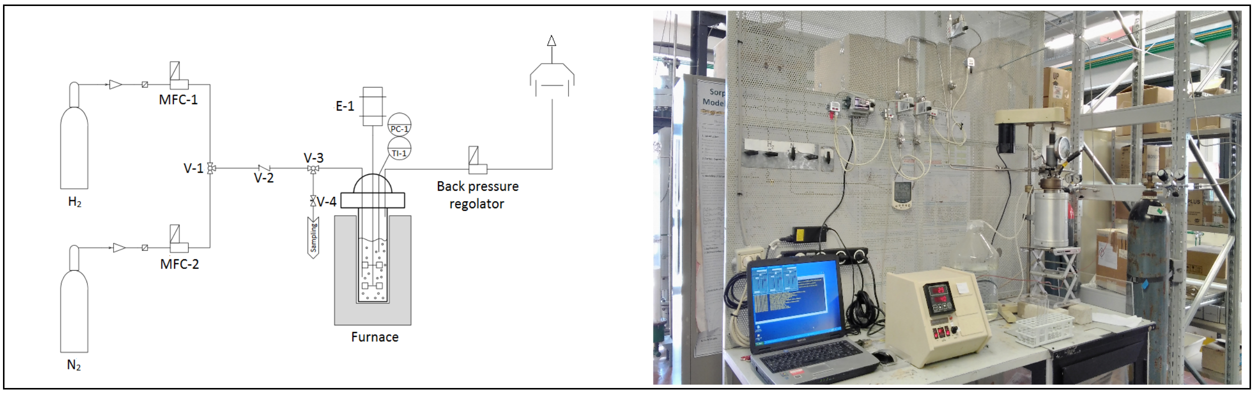

Figure 1 Hydrogenation plant scheme and the implementation with all the instruments: PC control unit, Mass Flow Control Bronkhrost Prestige, 3) TIC furnace, 4) Reactor and furnace, 5) Back Pressure reducer

The lab scale plant mainly consists of a batch reactor of 600 mL (Parr Reactor 4560), and the tests are carried out in a pure hydrogen atmosphere in the range of 4 - 12 bar and 60 - 180 °C. The duration of the test is adapted in accordance with the pressure and the temperature of test between 3 h and 6 h, respectively for the more and the less severe conditions. The reactor is charged with 180 g of rapeseed oil or FAME (around 200 mL) and with different mass catalysts/oil ratios of the reduced copper catalyst. The reactor is purged with nitrogen in order to eliminate all the air contained in the oil and the reactor, and brought to the test conditions with nitrogen. When the test conditions are reached, the hydrogen is fed in the reactor and, at established time, sampling is performed. Blank test with no catalyst has been also performed.

The samples withdrawn from the reactor are trans-esterified following IUPAC Standard and analyzed in a Varian 3400 GC equipped with a SUPELCO 2380 capillary column and a FID detector.

3. Results and discussion

The catalysts already produced show a good area respectively 261 m^2/g for the one produced with AE method and 163 m^2/g for the HP method. The catalysts shown two different pores dimensions, the first one 3-6 nm bonded to catalyst porosity and one bigger between 40-60 nm due to channeling between different particles of SiO_2. High area with pore of this dimensions is characteristic of amorphous silica and is in line with the results of Yuyun et al. (2017) [6] and Liang-feng et al. (2008) [7]. To augment area, it will proceed lowering aging time of the catalysts and changing some other parameters of the synthesis as pH and temperature of reaction.

The campaign of tests is in progress, performing the same operating conditions of the tests carried out with commercial Lindlar catalyst in our previous works [4][5]. Other different conditions (up to 200 °C and 25 bar) will be investigated to deepen the behavior of materials considered of interest and find the best operating conditions.

Spent catalyst collected will be then reused in coming tests to see the catalyst activity after repeated reactions, and it will be again characterized after tests. Furthermore, the comparison between tests with oil and tests with the methyl esters will be considered.

4. Conclusions

Synthesis and characterization of a new selective hydrogenation Cu-based catalysts are carried out. Tests with Lindlar commercial catalysts are complete and the performance of the new ones will be compared. At the end of test campaign, kinetic studies and modelling of this batch reactor will be developed and the optimal operating conditions will be defined.

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Keywords
“Vegetable oils”, “FAME”, “Selective Hydrogenation”, “Batch Reactor”.