

**Ramin Maghrebi<sup>1</sup>, Edoardo Miliotti<sup>1,2</sup>, Lorenzo Bettucci<sup>2</sup>, Marco Buffi<sup>2</sup>, Paolo Bondioli<sup>3</sup>, David Chiaramonti<sup>1,2</sup>**

<sup>1</sup> Department of Industrial Engineering, University of Florence, Italy – [ramin.maghrebi@unifi.it](mailto:ramin.maghrebi@unifi.it)

<sup>2</sup> RE-CORD, Renewable Energy Consortium for Research and Demonstration, Florence, Italy

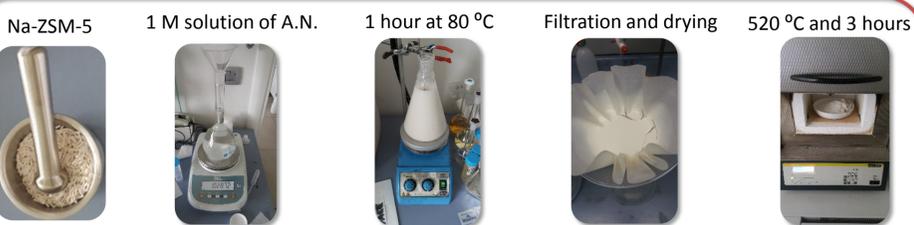
<sup>3</sup> Innovhub Stazioni Sperimentali per l'Industria S.r.l., Via Giuseppe Colombo, 79, 20133, Milan, Italy

## AIM

Long chain branched fatty acids have been attracting increasing interests due to their widespread applications in cosmetics, lubricant, surfactant, coatings, hydraulic fluids, and biodiesel industries. To upgrade these sustainable feedstocks, isomerization has been considered as one of the most promising alternatives. In previous researches, isomerization of saturated compounds has been carried out by porous solid catalysts doped with noble transition metals. However, isomerization of these compounds by utilization of non-noble metals could be a fascinating alternative. With this in mind, we tried to take advantage of the data available on isomerization of saturated short and long chain hydrocarbons due to the similarities with fatty acids. As a result, a set of experiments were carried out with hexadecanoic acid and HZSM-5 doped with iron salt under hydrogen atmosphere in a batch tubular reactor at different temperatures and reaction times (240 – 280 ° C; 2 – 6 h). Analysis of the products revealed the presence of iso-palmitic acids as the main products. This work proved that hydroisomerization of saturated fatty acids could be done by utilization of porous solid acids doped with non-noble metals. Moreover, this study demonstrated the difficulty of exploitation of non-noble metals due to extremely low conversions and selectivities.

## MATERIALS & METHODS

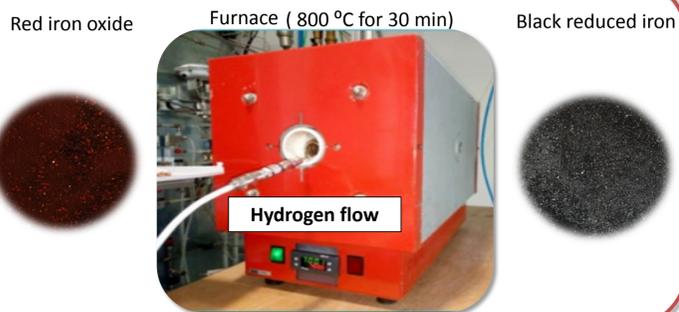
### Ion exchange



### Wet Impregnation



### Reduction of metal



### Experimental set-up



### Materials

Ion exchange	Impregnation
Triplicate	Wet impregnation(7%)
Na-ZSM-5, SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> : 38 from <b>ZEOLYST</b>	H-ZSM-5 from previous step
Ammonium Nitrate 99% From <b>Sigma Aldrich</b>	iron salt : Iron III Nitrate Nanohydrate From <b>Sigma Aldrich</b>
10 ml A.N./ 1 g ZSM-5	Isopropyl alcohol From <b>Sigma Aldrich</b>

## RESULTS & DISCUSSION

### Different conditions and their effects

*	Temperature [°C]	Reaction time [h]	Number of acidity [mg KOH/gr sample]	Melting point [°C]
T <sub>1</sub>	240	6	218	62.8
T <sub>2</sub>	250	6	217	62.8
T <sub>3</sub>	260	6	217	62
T <sub>4</sub>	270	6	217	61.5
T <sub>5</sub>	280	6	216	60.5
T <sub>6</sub>	280	2	218	62.8
T <sub>7</sub>	280	4	218	62.5

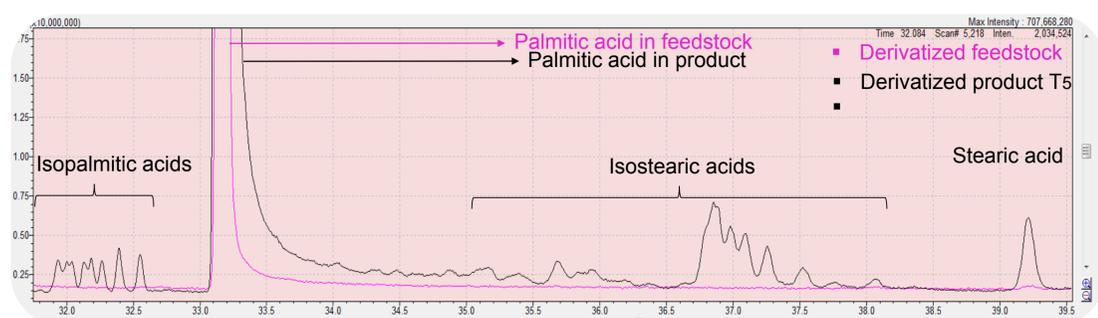
\*For all tests:

- 10 g palmitic acid was loaded into the reactor as the feedstock
- 1 g Fe H-ZSM-5 was loaded as the catalyst
- Heating rate was 28 ° C/min
- Hydrogen was selected as the atmosphere gas with the pressure of 6 bars
- Catalyst was calcined at 550 ° C for 3 hours before every tests
- Catalyst was used as powder

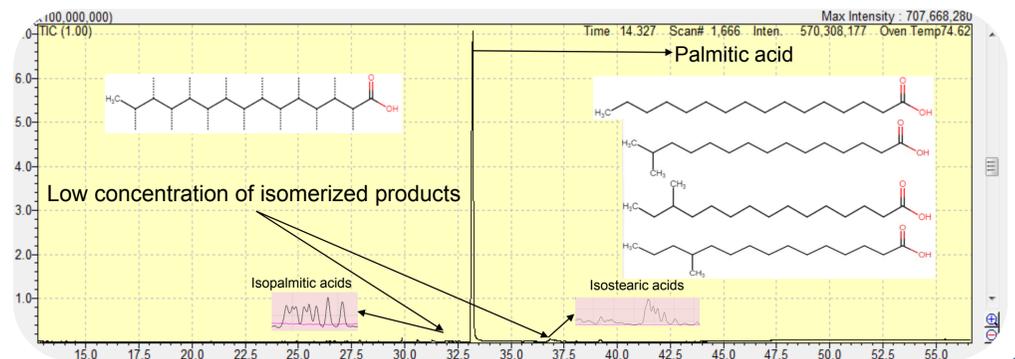
### Results from MP and number of acidity

- Melting point was used as an indicator for isomerization, therefore T<sub>5</sub> was screened for further analysis with gas chromatography.
- Measurement of number of acidity after every test demonstrated that almost no decarboxylation, decarbonylation or hydrodeoxygenation happened in the range of selected temperatures and reaction times.

### GCMS results for T<sub>5</sub>



- Production of isopalmitics was achieved as the first goal. This can be seen on the left-hand side of the hexadecanoic peak.
- Another considerable point is production of stearic acid and its isomers which can be seen on the right-hand side of the palmitic acid peak.
- Without derivatization, detection of isomers was impossible
- Derivatization was performed by BSTFA kit and isomer picks detected
- Concentration of desired products was very low.



## CONCLUSIONS

- This research demonstrates that hydroisomerization of SFAs by non-noble transition metals such as iron is possible.
- Great selectivity of the catalyst towards isomerized products (Isopalmitic and isostearic acids)
- Derivatization turned out to be vital, as the isomerized products were not detectable without it.
- Last but not least, the process suffers from extremely low conversions. To resolve that, longer reaction times, agitation, and higher pressures of hydrogen are the elements that could be useful for the future research to enhance the conversion of palmitic acid as a model compound to its desired isomers.

## ACKNOWLEDGEMENTS

1. University of Florence in Florence, Italy and Innovhub Stazioni Sperimentali per l'Industria in Milan, Italy for the financial support through the Ph.D. program.
2. RE-CORD, Renewable Energy Consortium for Research and Demonstration, for generously allowing us to utilize their well equipped laboratory.