A novel catalyst for hydroisomerization of hexadecanoic acid

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Summary

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. However, few researches have addressed the issue of isomerization of saturated carboxylic. Ferrierite zeolite with silica to alumina ratio of 20 was selected as a support. Moreover, platinum was selected as a promising dehydrogenating/hydrogenating agent. After all, a set of experiments were carried out with palmitic fatty acid under hydrogen atmosphere and zeolite ferrierite doped with .5 wt% platinum in a stirred autoclave engineering Parr at different temperatures and reaction times (240 – 320 ˚C; 2 – 16 h). Analysis of the products revealed the presence of isopalmitic. This work proved Platinum doped Ferrierite as a novel catalyst for hydroisomerization of palmitic acid as a model compound for saturated fatty acids in the vegetable oil.

Materials & Methods

Pre-calcination

Ammonium-Ferrierite → 550 °C and 12 hours → H-Ferrierite

Impregnation

Preparation of solution → Addition of solution → Formation of paste

Calcination

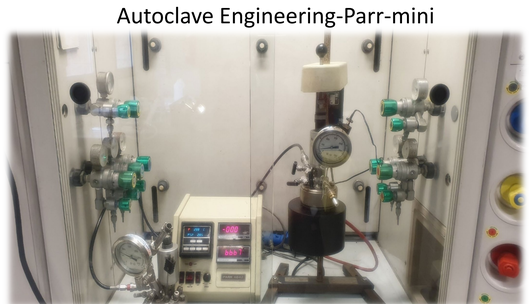
Evaporation of solvent → Removing extra compounds

Reduction of metal

White unreduced cat. → Furnace (480 °C for 3 hr) → Gray reduced cat.

Experimental set-up

Autoclave Engineering-Parr-mini



P_{max} [bar]	T_{max} [°C]	Vol(ml)
200	350	160

Materials

Catalyst support	Precursor
Ammonium-Ferrierite, SiO_2/Al_2O_3 : 20, CP 914C, ***ZEOLYST***	Tetraammineplatinum(II) Chloride Hydrate,98 wt% ***Sigma Aldrich***
Catalyst for derivatization	**Derivatizing agent**
Pyridine anhydrous, 99.8% ***Sigma Aldrich***	BSTFA, Derivatization Grade ***Sigma Aldrich***

Experiments & Results

Different operating conditions

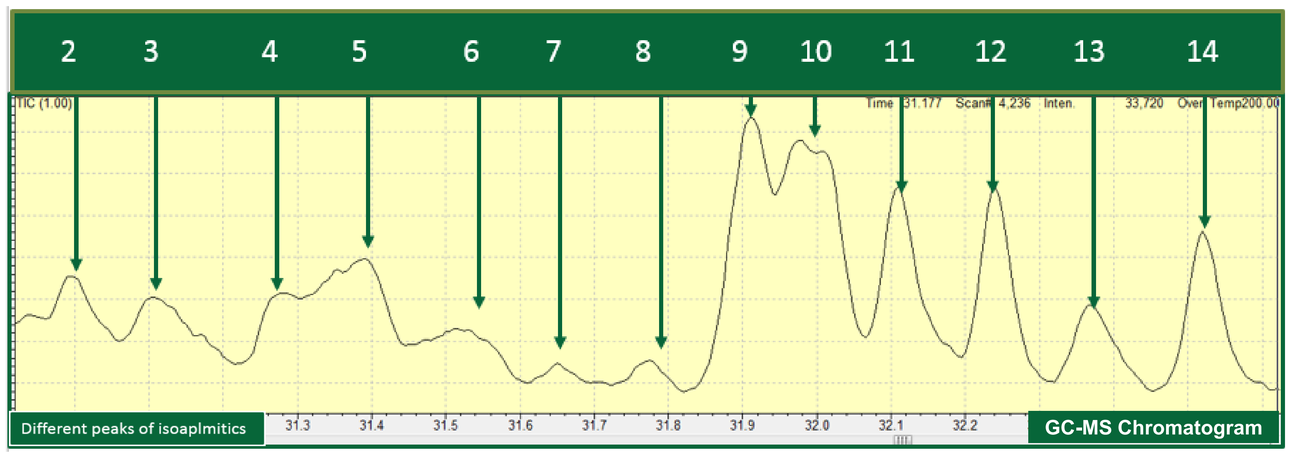
Experiment's code	Cat./Feed ratio(wt%)	H2 Pressure (bar)	Temperature(°C)	Reaction time(h)
Res 19.23.010	20	6	240	2
Res 19.23.011	10	6	260	4
Res 19.23.012	20	6	280	14
Res 19.23.013	6.5	40	300	8
Res 19.23.014	5	40	320	10
Res 19.23.015	7	40	310	6
Res 19.23.016	30	6.8	270	12
Res 19.23.017	22	40	285	16
Res 19.23.018	29	6.8	295	4.5
Res 19.23.019	25	40	240	16

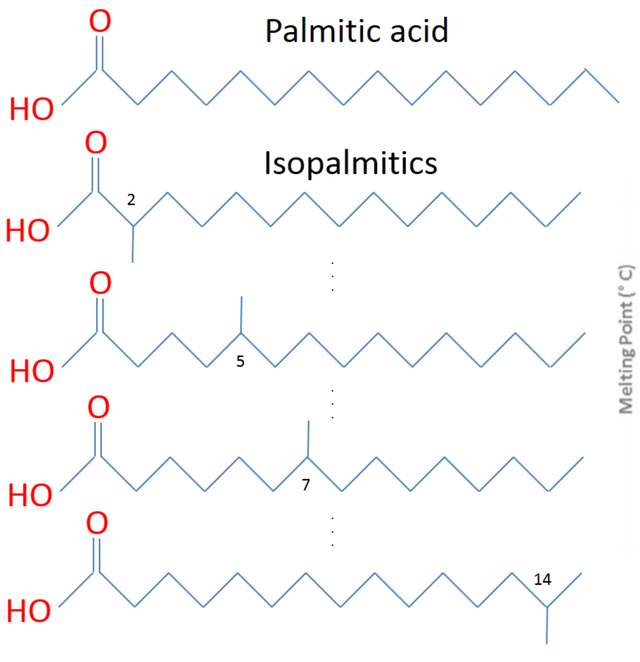
* For all experiments:
- 50 g palmitic acid was loaded into the reactor as the feedstock
- Stirring was set at 600 rpm Heating rate was 10 ˚ C/min
- Hydrogen was injected when the autoclave reached at 95 % of the T set point
- Catalyst was used in powder form

Extraction & Analysis method

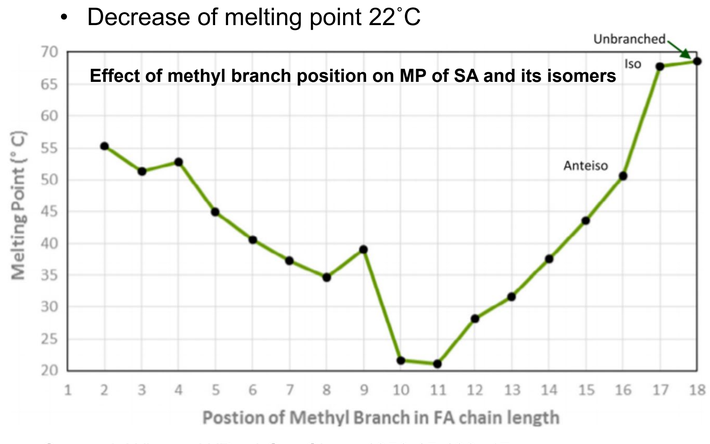
- After every experiment, the mixture of product and catalyst was at the solid state. This mixture was mixed with acetone and heated up to facilitate dissolving the product in the solvent.
- Then, vacuum filtration was used to separate solution from solid catalyst.
- Next, reduced pressure distillation was exploited to extract the product from acetone.
- Afterwards, BSTFA agent was used to derivatize the fatty acids to a sylilated form. Pyridine, was used after BSTFA addition, to promote solubility and catalyze the reaction.
- Finally, a GC 2010 with a GCMS-QP2010 mass spectrometer,(Shimadzu) equipped with a ZB-5 MS column 30m x 0.25mm x 0.25um (Phenomenex) was used to analyze the compounds.

Result & Discussion





- Yield of isomerized products based on Palmitic acid calibration= 36 wt%
- Selectivity towards isopalmitics: 85 wt%
- Conversion of PA: 58 wt%
- Decrease of melting point 22˚C



Cason J, Winans WR., J Org Chem 1950;15:139–47

Conclusion

- This research demonstrated that hydroisomerization of SFAs by Ferrierite zeolite doped with 5 wt% Platinum could be a solution for improvement of cold flow properties of biodiesel, due to a remarkable decrease in melting point, in comparison with the starting material.
- Significant selectivity of the catalyst towards isomerized isopalmitics products obtained.
- Derivatization turned out to be vital, as the isomerized products were not detectable without this method.
- Future work will be focused on developing more bi-functional micro/mesoporous catalysts to improve the yield and selectivity.

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