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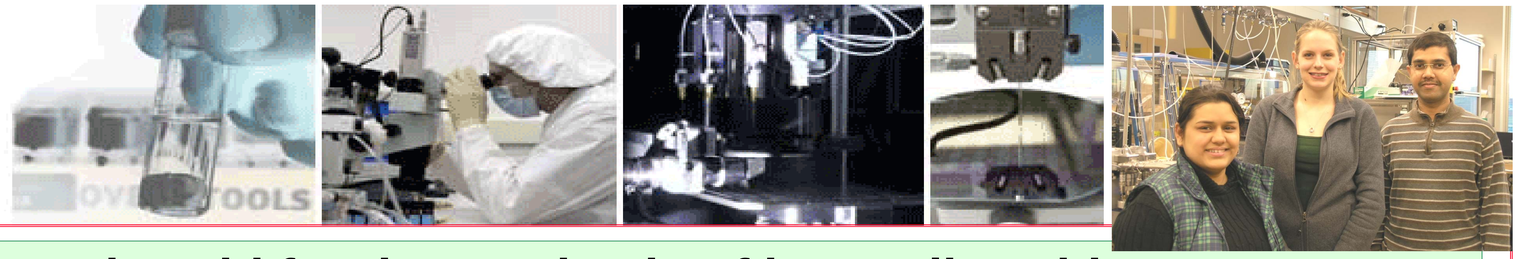

Oxidative cleavage of erucic acid for the synthesis of brassylic acid

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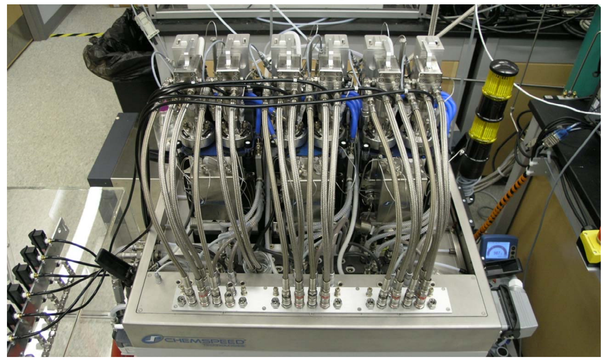
Objective of the Work

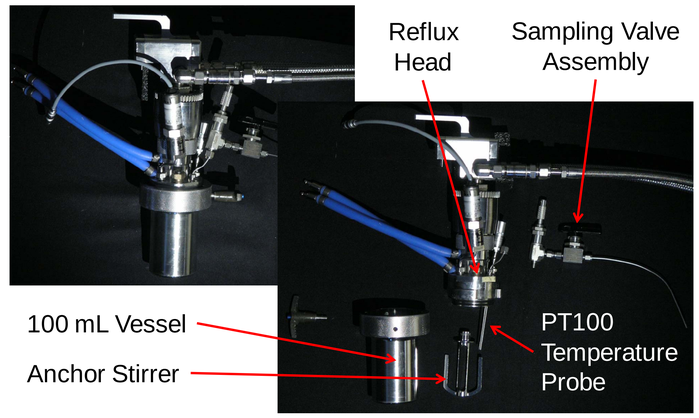
The main focus of this work is to synthesize Brassylic Acid (BA) using oxidative cleavage of Erucic Acid (EA).

✓ Crambe (Crambe abyssinica) is an industrial oilseed grown in North Dakota.
✓ Crambe has potential as an industrial fatty acid feedstock as a source of Erucic acid (EA). It has approximately 50-60 % of EA, a C_{22} monounsaturated fatty acid.
✓ Oxidative cleavage of unsaturated fatty acids derived from oilseeds produces long chain (9, 11, and 13 carbon atoms) dibasic and monobasic acids.
✓ These acids are known commercial feedstocks for the preparation of nylons, polyesters, waxes, surfactants, and perfumes.
✓ Other sources of EA are Rapeseed seed oil which has 50-60 % of EA. Rapeseed is grown outside USA.

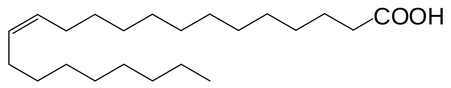
Chemspeed M106 Miniplant System and Individual Reactor



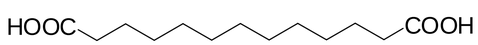
Features of M106: - 100 mL Reactor Size, - 6 Separately controlled reactors, - Temperature range of -20°C to 250°C, - Stirrer speed of 50 rpm to 1200 rpm, - Pressure control from 2 bar to 80 bar



Erucic Acid (EA)
$C_{22}H_{42}O_2$

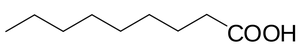


H_2O_2, *tert*-butanol, H_2WO_4
Molecular Oxygen, 80 °C



Brassylic Acid (BA)
$C_{13}H_{24}O_4$

+



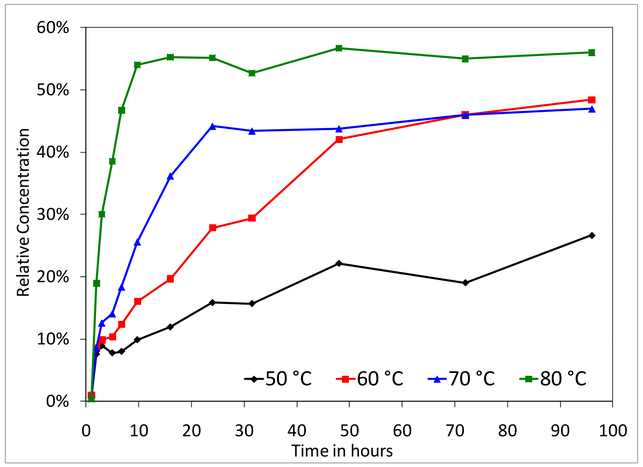
Nonanoic Acid (NA)
$C_9H_{18}O_2$

Overall Reaction

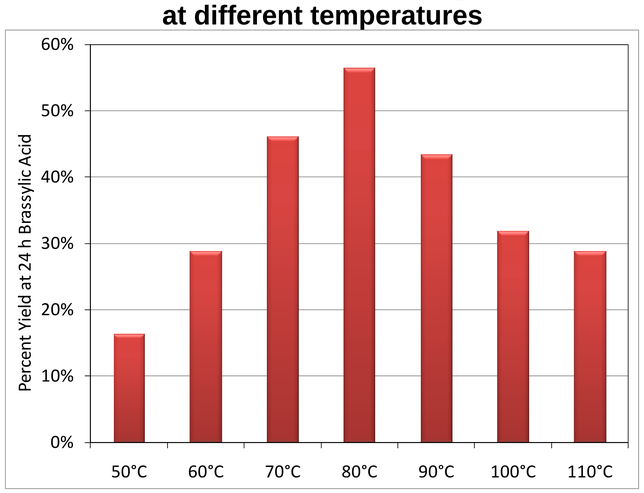
$C_{22}H_{42}O2 + 2O_2 \longrightarrow C_{13}H_{24}O_4 + C_9H_{18}O_2$

Erucic Acid (EA, MW = 338), EAOMe, MW = 352
Brassylic Acid (BA, MW = 244), $BA(OMe)_2$, MW = 272
Nonanoic Acid (NA, MW = 158), NAOMe, MW = 172

BA conversion vs time at 10 bar O_2



Percent yield of BA at 10 bar O_2 pressure at different temperatures



Variables Studied Using M106 Reactor

✓ Reproducibility check (parallel reactors) Vs tradition round bottom flask – Both gave good yields of BA.
✓ O_2 Pressure (10 bar) / O_2 bubbling – Both gave good yield of BA.
✓ Different O_2 pressure did not have any effect in BA yields.
✓ Concentration of catalyst – 0.1 moles of catalyst w. r. to EA gave high yields.
✓ Different catalyst (WO_3, H_2WO_4, Peroxo form of H_2WO_4) - H_2WO_4 gave high yield.
✓ Large scale synthesis and optimization – In progress

Conclusions

✓ The oxidative cleavage of EA was done using a high throughput parallel pressure reactor system.
✓ Kinetics of the reaction shows that BA yields reach a saturation at 12 hours.
✓ H_2WO_4 was found to be the best catalyst for the oxidative cleavage of EA .
✓ High yields of BA were obtained at 80 °C with bubbling of O_2 or 10 bar of O_2 for 12 hours.

Future work

Characterize BA thoroughly. To make large batch of brassylic acid.

Characterization of Brassylic Acid

✓ Gas chromatography-mass spectrometry (GCMS)
✓ Melting point by differential scanning calorimetry (DSC)
✓ MP of EA = 29 °C, BA = 114 °C and NA = 9 °C
✓ X-ray diffraction (XRD) for purity and phases
✓ X-ray fluorescence (XRF) for W content
✓ Nuclear magnetic resonance (NMR)
✓ Gel permeation chromatography (GPC) for any oligomerization
✓ Elemental Analysis (CHNS) for purity

References

1) Sibi, Mukund P.; Boudjouk, Philip; Ji, Jianguo, Method for preparation for carboxylic acids. U.S. Patent 5,939,572, Aug 17 1999.
2) Venturello, Carlo; Ricci, Marco; Process for the preparation of carboxylic acids starting from olefines or vicinal dihydroxy compounds. U.S. Patent 4,532,079, July 30 1985.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, under Grant DE-FG36-08GO88160. The authors would like to gratefully acknowledge US DOE. The authors also thank Materials Characterization and Analysis Laboratory (MCAL) team of CNSE.

The effort undertaken is sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy and any opinions, finding, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Office of Energy Efficiency and Renewable Energy.