TechEx.in
Tech Transfer Hub

CSIR-Central Salt & Marine Chemicals Research Institute

Match Maker/ Renewable Chemicals & Materials/ 9 Apr 2021

Process for manufacturing γ-Valerolactone (Gvl) from Levulinic Acid (LA)

Lead Inventor: Dr Kannan Srinivasan

Organization: CSIR-CSMCRI, Bhavnagar

TechEx.in Case Manager: Devanshi Patel (devanshi@venturecenter.co.in)

TechEx.in is a Regional Tech Transfer Office supported by:

birac Ignite Innovate Incubate

nbm NATIONAL BIOPHARMA MISSION innovate in India for inclusiveness (i3)

VENTURE CENTER

The Opportunity

Gvl as a high-boiling "green" solvent:

- Green, high-boiling solvent for high temperature reactions (>100 C)
- Better alternative for GBL - used in polymers, cosmetics, pharma and solar cell industry
- Alternative to ketone solvents (including cyclic/ heterocyclic) like MIBK (Global market ~ 650 m$)
- Green and bio-solvents global market is ~7b$

Gvl as a food additive/ flavoring agent:

- Food flavours; Precursor of food additive
- Large application in China and Far East

Value added product from LA:

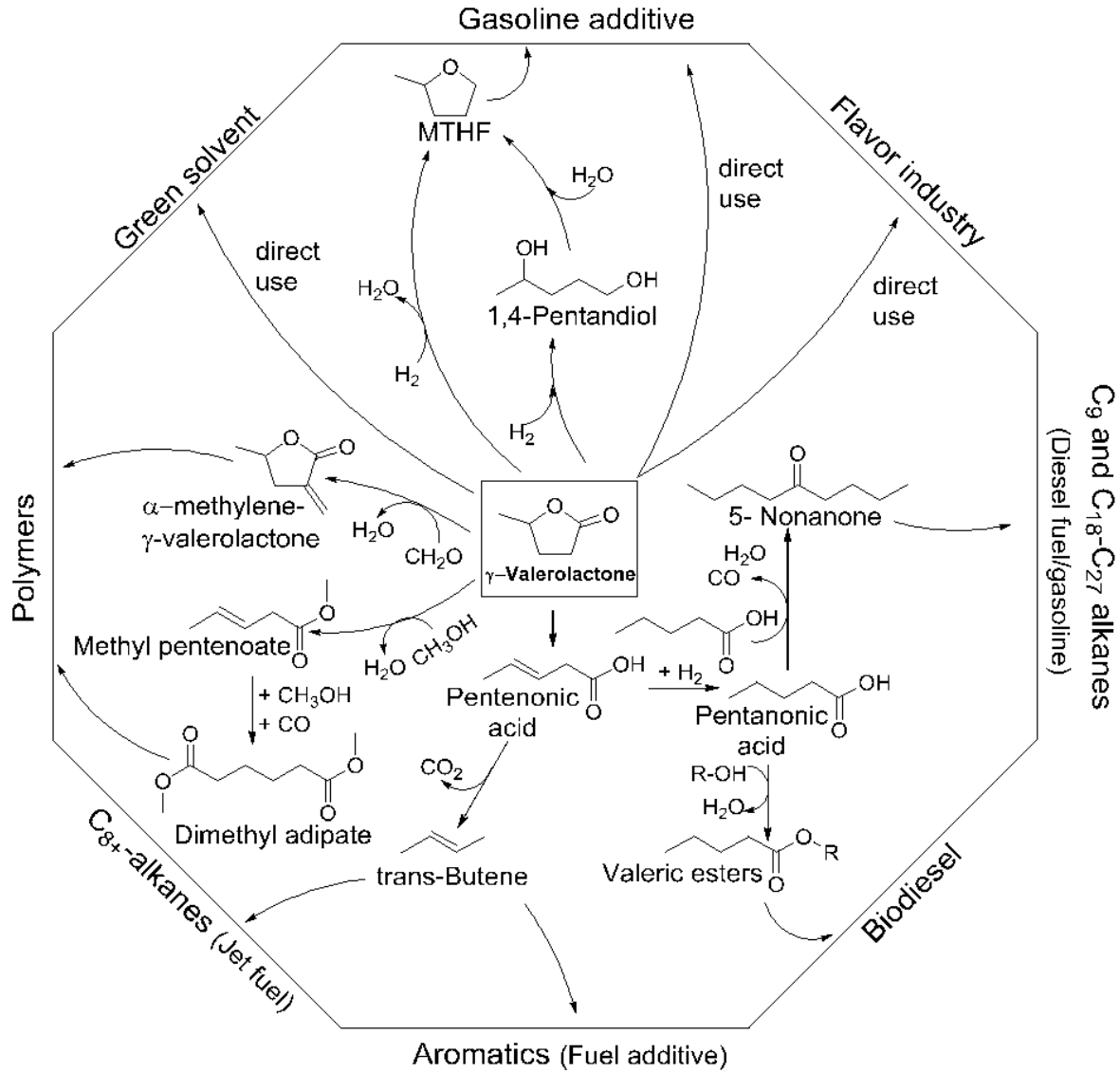
- Global LA market ~ 30 m$

Gvl as a fuel additive and bio-fuel of the future:

- Gasoline additive in green fuels and as an advanced biofuel with clean burning characteristics
- Biofuel market ~ 150b$

Other applications of Gvl:

- Pro-drug to GHV (similar to restricted GHB)
- Manufacturing biopolymers



Scheme 1: Use of GVL and its derivates. [20] – Reproduced by permission of The Royal Society of Chemistry.

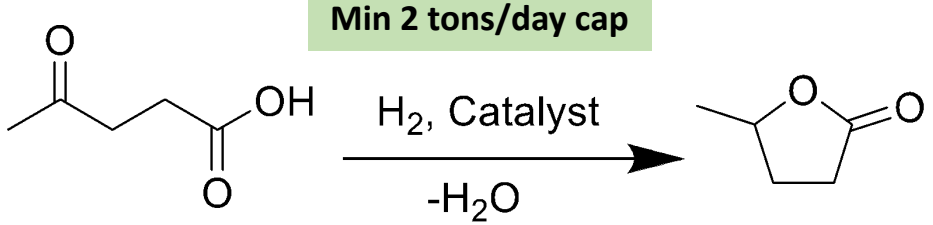
Ref: Konstantin Hengst, Sustainable Synthesis of γ-Valerolactone, PhD Thesis, Karlsruhe Institute of Technology (KIT), 2015.

Who should be interested and why?

Who?	Why?
Producers of high-boiling solvents	• Green solvent and suitable replacement for ketonic solvents • Better performance than GBL • Less toxic; oxidatively stable; easier to transport; definite acceptable smell
Producers of Levulinic Acid	• Higher value end products (Gvl)
Producers of Gvl	• More cost-effective process
Bio-refineries	• Additional value addition chain
Biofuels producer	• Fuel additive and future fuel

About the technology

Min 2 tons/day cap



Levulinic acid

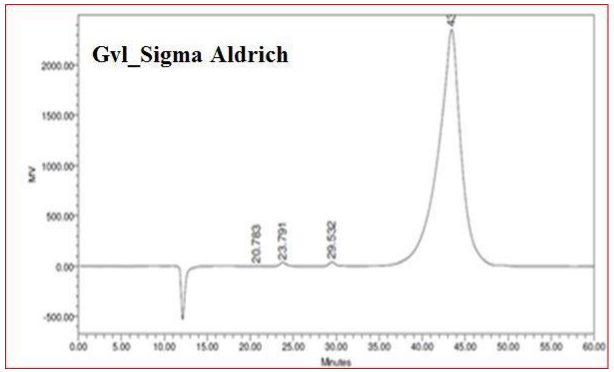
Cost: Rs X/kg
Cost: USD Y/kg

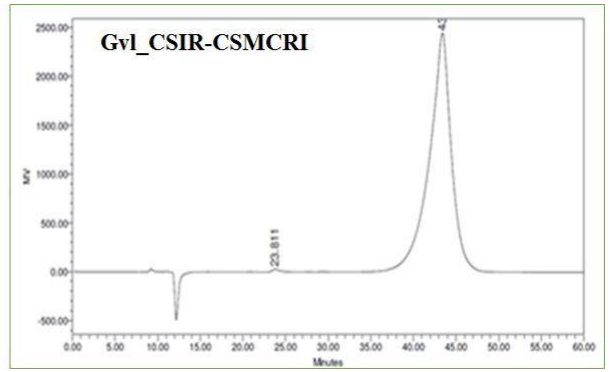
γ–valerolactone

Cost: Rs (X+200) /kg
Cost: USD (Y+3)/ kg

Process technology features:

- Reaction under mild conditions (50-100 C, 5-15 atm H_2)
- 100% conversion of LA
- Excellent selectivity of GVL even at high LA concentration
- Lesser reaction time
- Using lesser quantity of precious metal catalyst
- In situ generated catalyst (no prior reduction step)
- Recyclable active catalyst; catalyst can be supported on inexpensive supports
- Reaction in aqueous medium
- Stoichiometric quantity of hydrogen used ⇒ avoids recycling operations
- Continuous flow hydrogenation process also shown





CSMCRI's Gvl is of high quality and free of impurities

Current status

Technology status:

- Demonstrated at 1 Liter scale (lab)
- Patent protected
- Techno-economic viability analysis done – Viable at > 2 tons/ day scale and 2 shifts

Patents:

- Priority document: 2866DEL2014 (8 Oct 2014)
- Coverage: IN, US, EP
- Granted: US 10221149B2, EP3204366B1; Pending: IN

Publications:

- Hydrous ruthenium oxide: A new generation remarkable catalyst precursor for energy efficient and sustainable production of γ-valerolactone from levulinic acid in aqueous medium, Sreedhar Gundekari, Kannan Srinivasan, Applied Catalysis A: General 569 (2019) 117–125 (link).
- Screening of solvents, hydrogen source, and investigation of reaction mechanism for the hydrocyclisation of levulinic acid to γ-valerolactone using Ni/SiO2-Al2O3 catalyst. Sreedhar Gundekari, Kannan Srinivasan, Catalysis Letters, 149 (2019) 215-227 (link).
- In situ generated Ni(0)@boehmite from NiAl-LDH: An efficient catalyst for selective hydrogenation of biomass derived levulinic acid to γ-valerolactone, Sreedhar Gundekari, Kannan Srinivasan, Catalysis Communications, 102 (2017) 40–43 (link).

Team & organization

केन्द्रीय नमक व समुद्री रसायन अनुसंधान संस्थान
CENTRAL SALT & MARINE CHEMICALS RESEARCH INSTITUTE
वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

Lead Scientist: Dr Kannan Srinivasan
Director, CSIR-CSMCRI

Humboldt Fellow (Germany)
JSPS-INSA Research Fellow (Japan)
Raman Research Fellow (USA)
CRSI Bronze Medal

Expertise: Heterogeneous catalysis in particular for fine and speciality chemicals and biomass based fuels and chemicals,, Environmental chemistry, Material science, Solid state chemistry

- CSMCRI is a constituent lab of the CSIR, India
- Track record of technology transfer & working with industry; attractive models of engagement and flexible terms for IP
- Publicly funded non-profit R&D lab & DSIR recognized SIRO => R&D project sponsors can claim tax benefits; Eligible for CSR support

- Key assets and strengths of Dr Srinivasan lab:
  - Team strength: **6**
  - **4 granted, 1 filed** US patent; **25** publications in biomass value addition
  - Well equipped labs and analytical facilities
    - Excl high pressure reactor lab; reactors capacity from 50 cc to 10 L with different MoC
    - State-of-art, sophisticated analytical infrastructure facility
    - XPS (X-ray photoelectron spectrometer) for surface characterization of solid catalysts
  - Pilot plant facility
  - Industry Sponsored projects like biomass derived chemicals for Jayant Agro

Next Steps

Proposed next steps:

- Technology licensing by licensing partner who has tied up LA supply and Gvl demand
- Setting up of pilot plant at client site
- Scale up to a target capacity of 2-5 tons/day

Seeking:

- Industrial partners interested in technology licensing; Industrial partner interested in putting up a pilot plant at their site; CSMCRI can provide hand-holding support
- CSMCRI is open to discussions on other models of engagement with industry partners

TechEx.in
Tech Transfer Hub

CSIR-Central Salt & Marine Chemicals Research Institute

For more information, contact:

Devanshi Patel
devanshi@venturecenter.co.in
+91-74100-45655

TechEx.in is a Regional Tech Transfer Office supported by:

birac
Ignite Innovate Incubate

nbm
NATIONAL BIOPHARMA MISSION
innovate in India for inclusiveness (i3)

VENTURE CENTER

γ-valerolactone – Properties & Features

Property	Value
CAS-No	108-29-2
Formula	$C_5H_8O_2$
MW (g mol^{-1})	100.112
Refractive index (n20/D)	1.432
Density (g mL^{-1})	1.05
Flash point (°C)	96
Melting point (°C)	-31
Boiling point (°C)	207–208
Solubility in water	Miscible; ≥100 mg/mL

Characteristic Features:

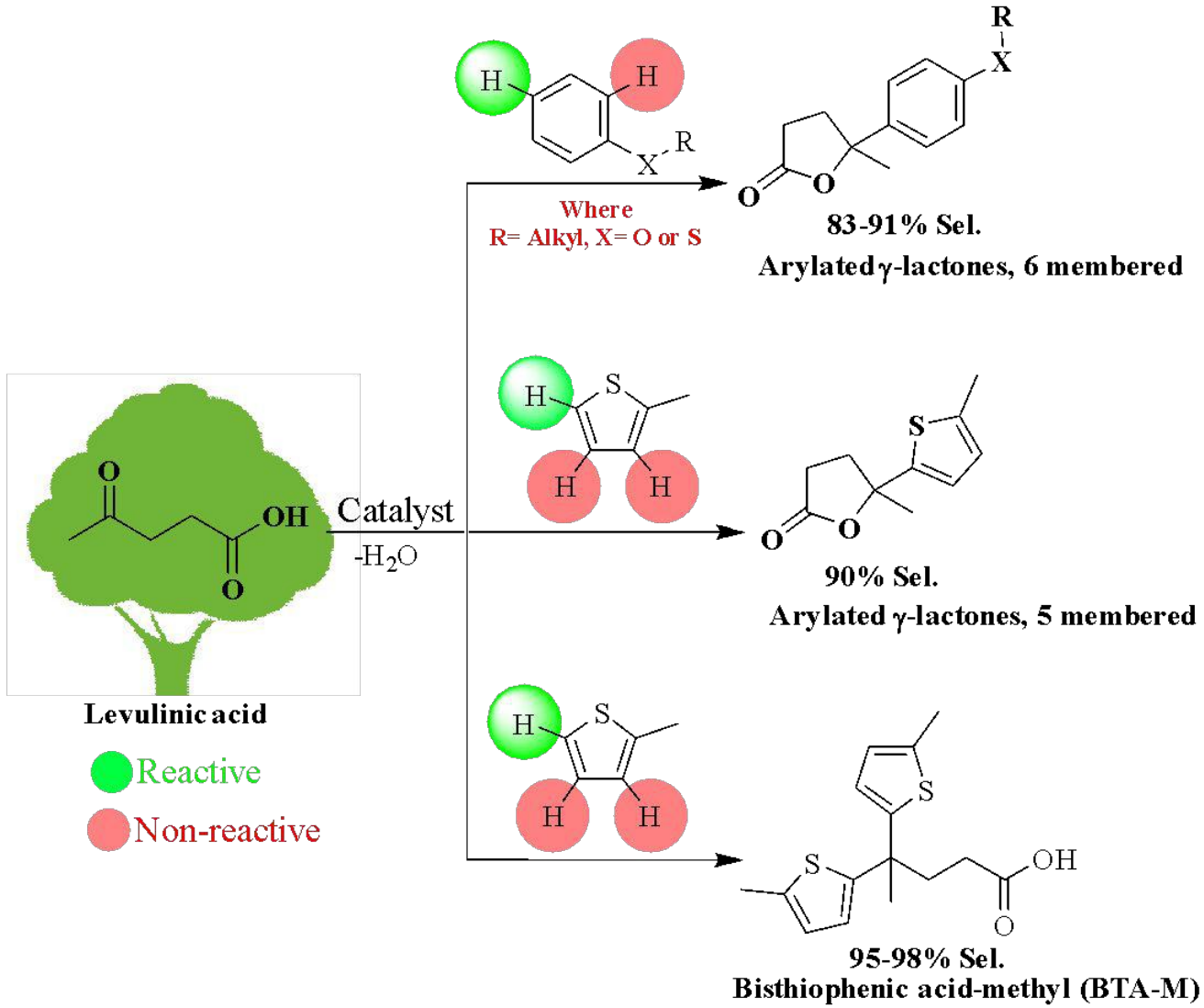
- Definitive acceptable smell (for easier recognition of leaks and spills)
- High solubility in water to assist in biodegradation
- Low vapor pressure (0.65 kPa at 25°C and 3.5 kPa at 80°C)
- Does not hydrolyse under neutral conditions
- Does not form measurable amount of peroxides in a glass flask under air in weeks (oxidatively stable & large scale use).
- Comparative fuel additive property as that of ethanol (but does not form azeotrope and hence easier and less energy demanding separation unlike ethanol)
- Fewer production steps to make compared to chlorinated solvents, THF and ionic liquids

Green Chem., 2008, 10, 1024-28
Green Chem., 2013, 15, 584–595

γ-valerolactone – As green solvent (comparison with other solvents)

- **g-valerolactone** is low toxicity towards humans and the environment; Price can be expected to drop very significantly in the near future (Green Chem. DOI: 10.1039/d0gc04353b).
- Potential replacement for dimethylsulfoxide (DMSO) and g-butyrolactone (GBL) in agrochemical formulations, where these solvents are used 30-70 wt% - US 0105073 A1 (2009), EP 1 023 833 A2 (2000); US 0130912 A1 (2013).
- Efficient medium for converting hemicellulose into furfural, cellulose/cellobiose into glucose, sugars to 5-hydroxymethyl furfural and levulinic acid; Angew. Chem. Int. Ed. 2013, 52, 1270-1274; Energy Environ. Sci., 2013, 6, 76-80, Green Chem., 2014, 16, 4659-4662.
- **g-valerolactone** reported as solvent for preparing polymer precursor solutions, used in engineering plastics. (ACS Sustainable Chem. Eng. 2015, 3, 1881-1889).
- Toxicity of the conventional solvents (N-methylpyrrolidin-2-one, N,N-dimethylacetamide, dimethylformamide, toluene, 1,4-dioxane, acetonitrile, and tetrahydrofuran) is significantly higher compared to g-valerolactone – ChemPlusChem 10.1002/cplu.201600389.
- Alternative safer solvent for various organic transformations: aminocarbonylation, synthesis of phosphatidylserine, and various coupling reactions such as Hiyama, Sonogashira, and Heck.
- **g-valerolactone** also shows better result as solvent medium for enantioselective hydroformylation compared with toluene. (ChemPlusChem-10.1002/cplu.201600389, Green Chem., 2012, 14, 1581, ACS Sustainable Chem. Eng. 2014, 2, 2461-2464, Green Chem., 2016, 18, 842-847, Green Chem.-10.1039/c4gc01728e, Green Chem.-10.1039/c4gc01677g.
- **g-valerolactone** is precursor for various polymeric monomers including e-caprolactam, a-methylene-g-valerolactone, g-hydroxy-amides, dimethyl adipate, etc. (ChemSusChem 2014, 7, 1984-1990, Applied Catalysis A: General 272 (2004) 249-256, Procedia Chemistry 4 (2012) 260-267, Chem. Commun., 2007, 3488-3490, Green Chem. DOI: 10.1039/c5gc01922b).
- **g-valerolactone is** used as an illuminating liquid in glass lamps for hours without the formation of noticeable smoke and/or odor. (ACS Sustainable Chem. Eng. 2015, 3, 1899-1904).
- **g-valerolactone** as a cleaning agent or/and solvent in various paint and coating formulations, as well as a solubiliser in cosmetics, pharmaceuticals, or agrochemicals. (Green Chem. DOI: 10.1039/d0gc04353b).

Levulinic acid-based arylated derivatives

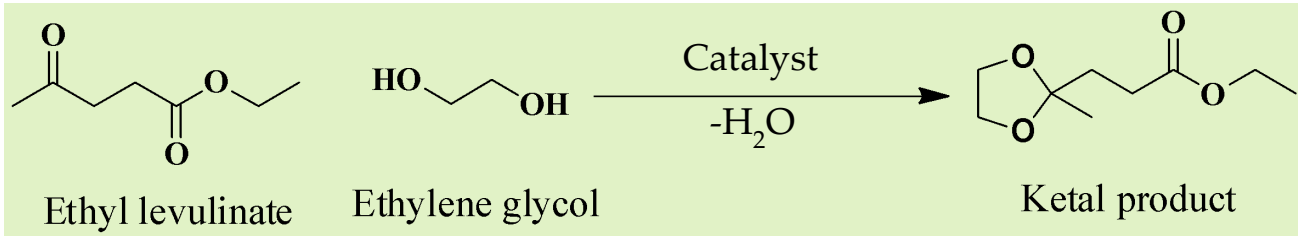


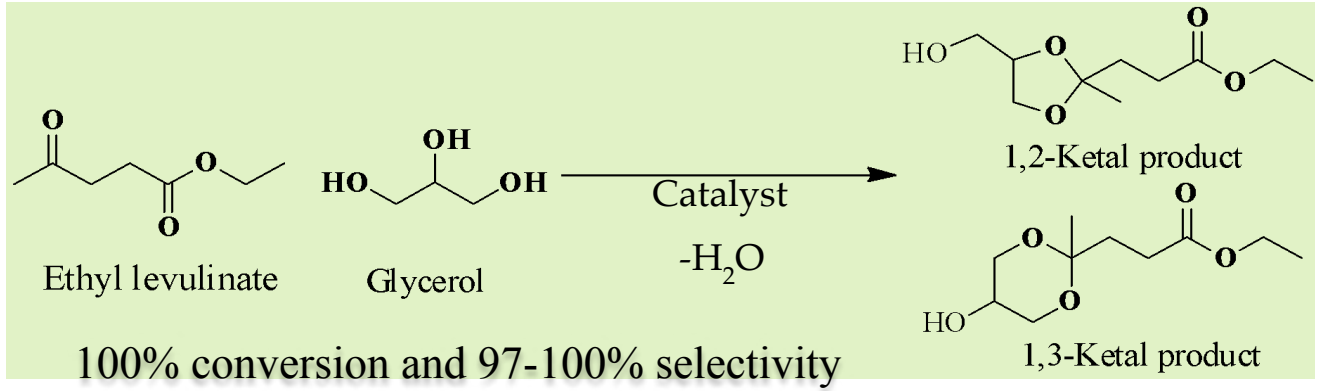
Advantages

- Mild reaction conditions (85-150 °C)
- Reactions under open atmosphere
- Good conversion and yields
- Use of recyclable heterogeneous catalysts
- Use of excess aromatic in the reaction medium that acts as solvent and enhance the kinetics of the reaction with excellent selectivity that could be recycled
- Good chemo- and regio- selectivity for the preparation of arylated g-lactones.
- Good selectivity (>95%) for the preparation of BTA-M along with total conversion of LA
- The prepared products of LA have structural accessibility to develop applications in the field of pharmaceuticals, agrochemicals and fuel industry.
- Some of the synthesized compounds are novel in nature, first time in the world.
- BTA-M showed good elasticity and mechanical strength with mixing of PVA and PVDF. BTA-M resulted better plasticizing ability as compared with bisphenol A (BPA), diphenolic acid (DPA), and dioctyl phthalate (DOP).

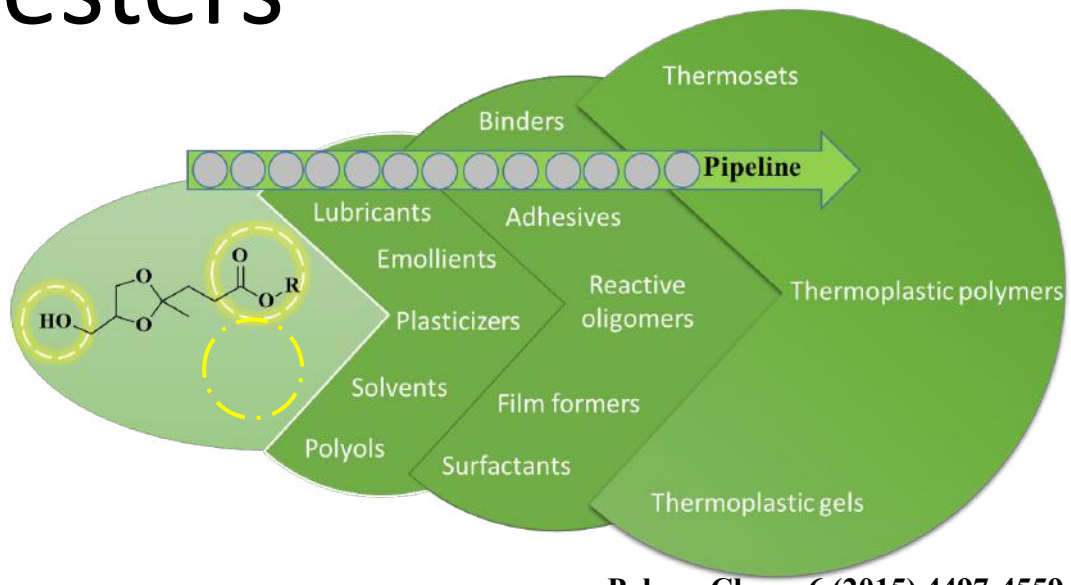
Indian Patent Office vide Appl. No. **201611023585** (11th July 2016); ChemCatChem, 2019, 11, 1102-1111

Levulinate based ketals and esters





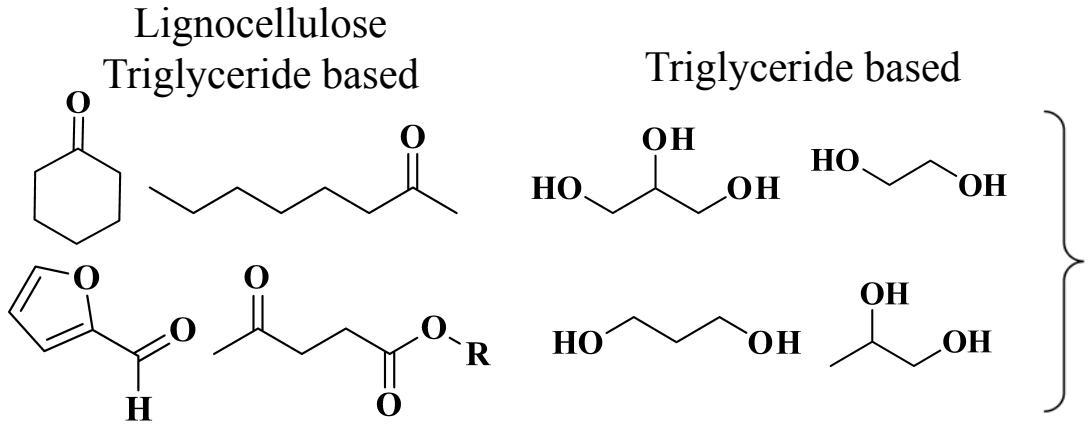
100% conversion and 97-100% selectivity

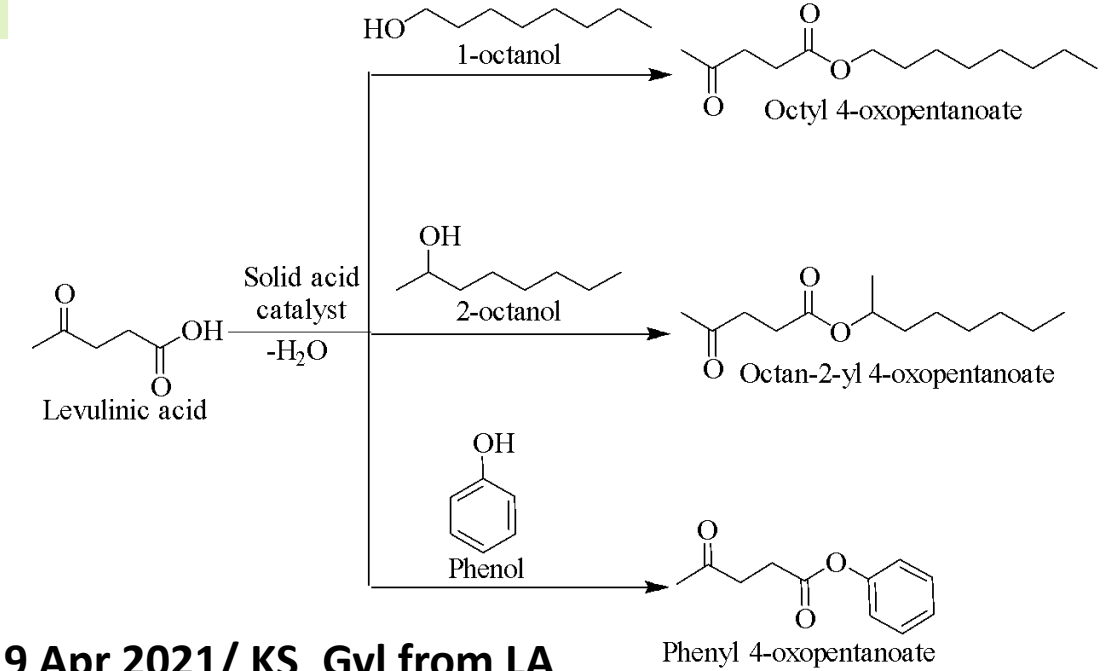


Polym. Chem. 6 (2015) 4497-4559

Our approach for ketal work

Use of heterogeneous catalysts and expanded reaction scope





References > Market data

1. https://www.gminsights.com/industry-analysis/methyl-isobutyl-ketone-market#:~:text=Methyl%20Isobutyl%20Ketone%20Market%20size,4%25%20from%202019%20to%202025.&text=Thriving%20global%20automotive%20sector%20has,product%20demand%20in%20the%20industry
2. https://www.expertmarketresearch.com/reports/methyl-isobutyl-ketone-market
3. https://www.marketwatch.com/press-release/global-green-and-bio-solvents-sales-market-size-2021---report-include-indepth-analysis-of-industry-share-price-expected-cagr-future-investment-current-trends-with-top-market-leaders-and-recent-developments-2021-01-07
4. https://www.thecowboychannel.com/story/43227015/gamma-valerolactone-cas-108-29-2-market-size-2021-by-top-countries-data-industry-analysis-by-regions-revenue-share-development-tendencies-and
5. https://www.thecowboychannel.com/story/43227015/gamma-valerolactone-cas-108-29-2-market-size-2021-by-top-countries-data-industry-analysis-by-regions-revenue-share-development-tendencies-and
6. https://www.psmarketresearch.com/market-analysis/levulinic-acid-market

7. https://www.globenewswire.com/news-release/2021/01/22/2162581/0/en/Biofuels-Market-Size-Worth-Around-US-307-01-Billion-by-2030.html
8. https://www.ebi.ac.uk/chebi/searchId.do;jsessionid=00475B786082AE69A27DF9A5F029655E?chebiId=48569&structureView=applet&viewTermLineage=#:~:text=GVL%20behaves%20as%20a%20prodrug,a%20legal%20substitute%20for%20GHB.