Valorization of Cashew Nut Shell Liquid (CNSL):

A Versatile Agro-waste Material

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Our Approach to Valorization of CNSL

Leveraging current eco-system and addressing call from Nation.

https://aatmanirbharbharat.mygov.in/

Fossil Resources *vs.* Biomass: A Perspective

CO_2

- Carbon Dioxide

1 year

New Carbon

- Biomass
- Agricultural Crops

Bio-chemical Industry

>10^6 years

Fossil Resources

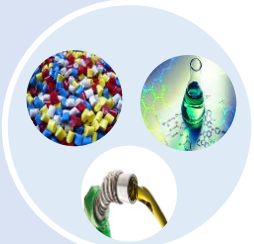
- Petroleum
- Natural Gas
- Coal

Chemical Industry

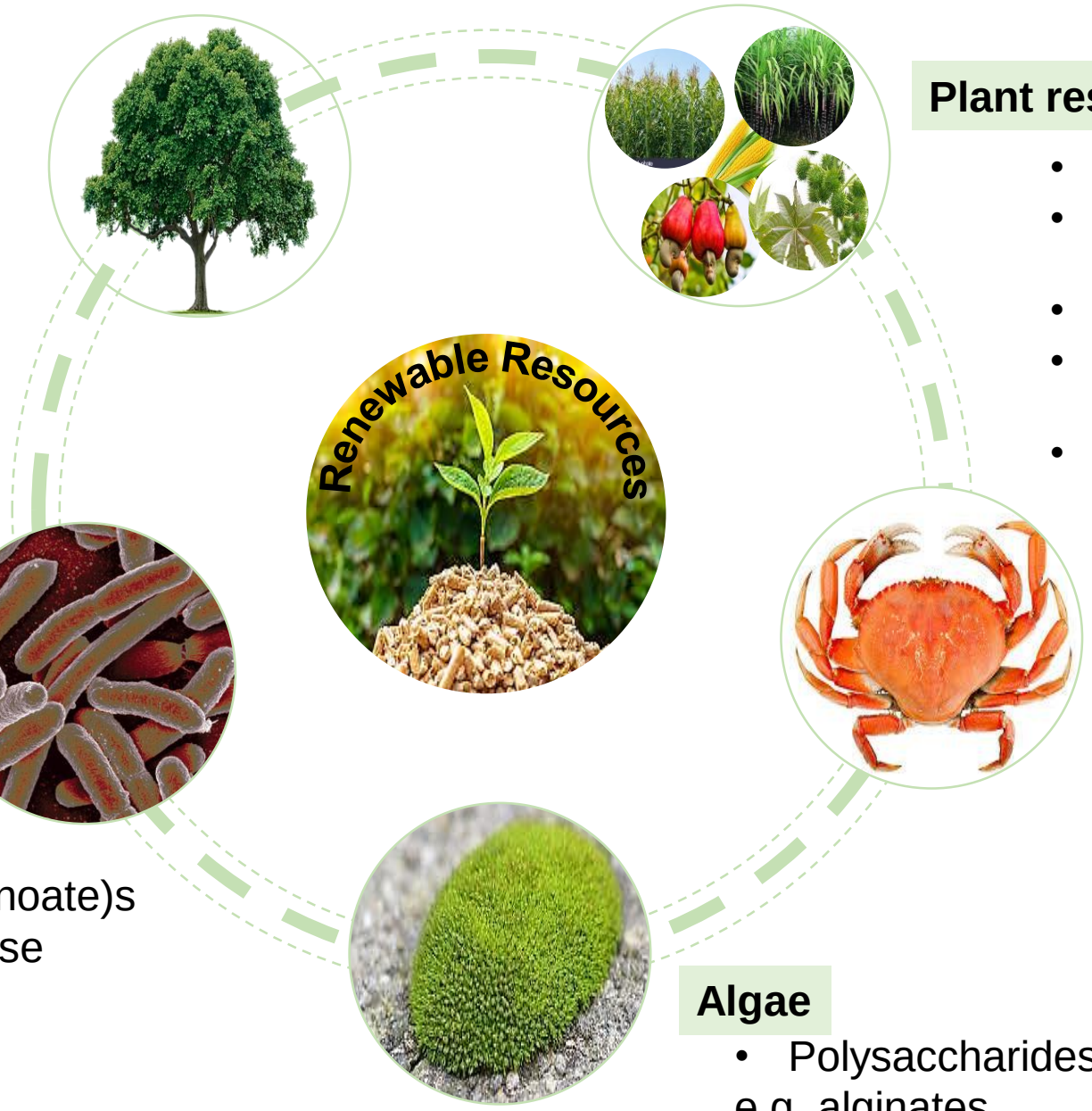
1 – 10 years

Chemical Resources

- **Polymers**
- Chemicals
- Fuels



Renewable Resources for Bio-based Building Blocks



Wood

- Cellulose
  (108 MMT/Y)
- Lignin
  (100 MMT/year)
- Hemicellulose
- Natural Rubber
  (14 MMT/year)
- Suberins
- Tannins
- Rosins
- Terpenes
  (4.0 MMT/year)

Plant residues

- Starch
- Vegetable oils
  (72 MMT/year)
- Hemicellulose
- Sugars
  (180 MMT/year)
- Natural Phenols
  - **CNSL (4.4 MMT/Year)**

Animal Residue

- Chitins and Chitosan
  (0.1 MMT/Year)
- Proteins

Bacterial Biomass

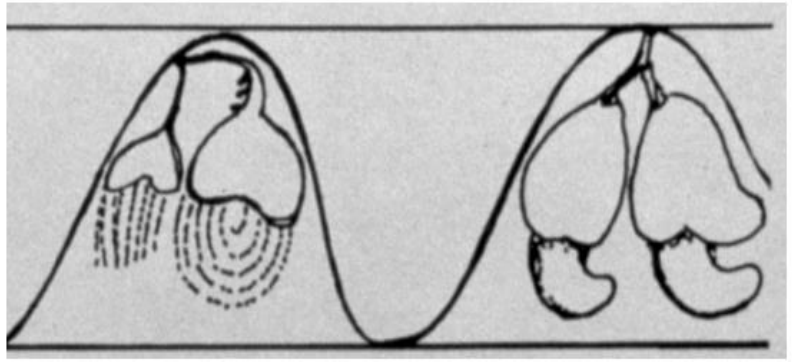
- Poly(hdroxyalkanoate)s
- Bacterial Cellulose

Algae

- Polysaccharides
  e.g. alginates

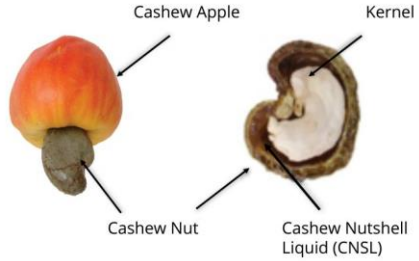
History: Cashew Nuts in India

It is generally believed that the Portuguese carried the cashew nut crop to East Indies, Africa and India in the 16th century, and the Spanish probably took it to the Central American countries and the Philippines.



Cashew nut is represented on the balustrade of the Bharhut Stupa in Madhya Pradesh, India, dating to the 2nd century BC (before 200 BC). (Photo of the sketch courtesy of the American Institute for Indian Studies, the copyright holder).

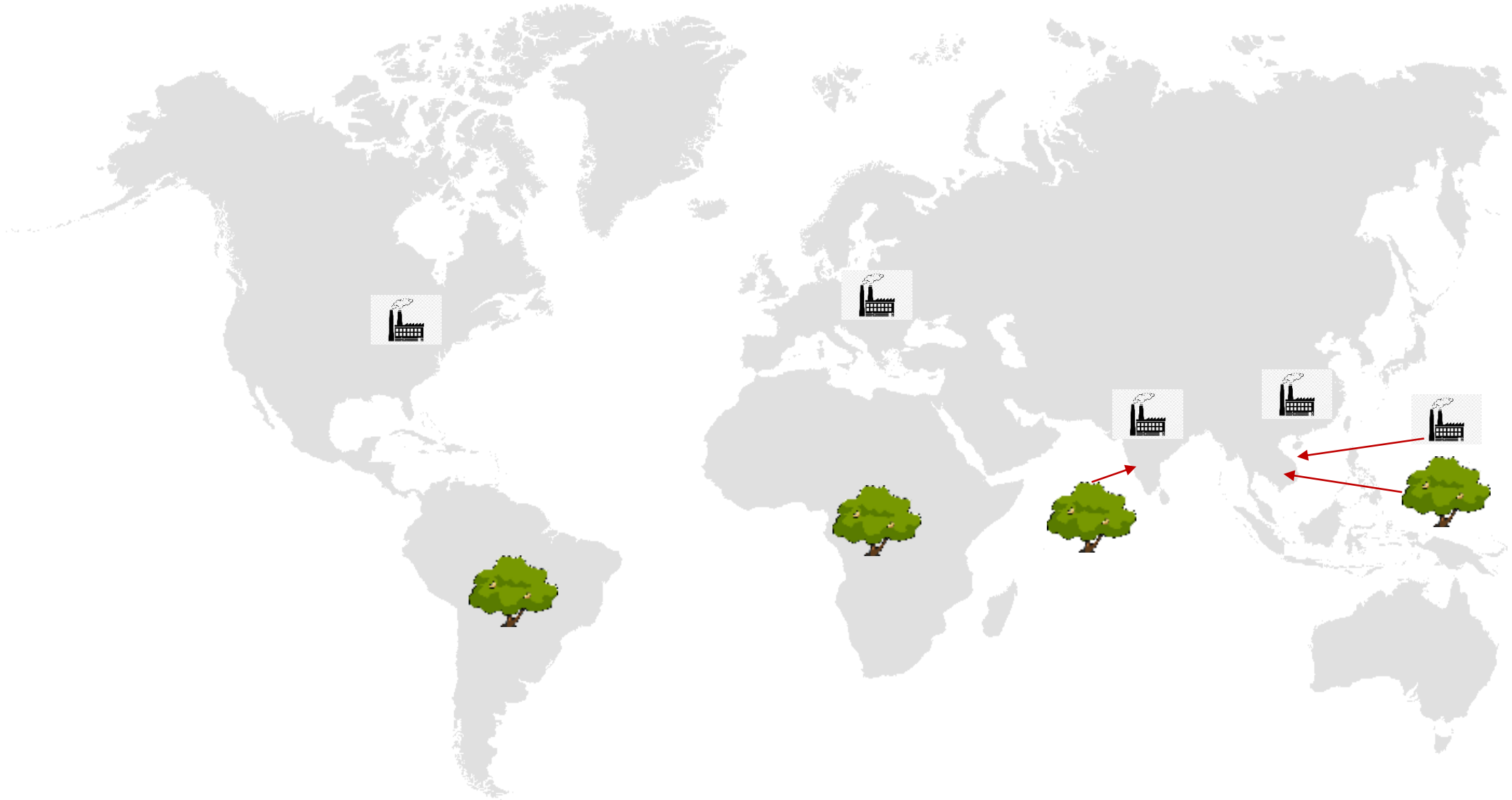
Depiction of complete plant of cashew with flowers and fruits on the pillars at the Jambukeshvara temple in Tiruchirapalli, Tamil Nadu, India, supposed to have been built 2500 years ago



Cashew Apple	~10 cm long
Cashew nut Shell	2.5 – 4 cm long
Cashew nut shell Thickness	3 mm
Kernel	20 to 25%
CNSL liquid	20 to 25%
Testa	2%

Anurudh K. Singh, ***Asian Agri-History****, 22 (3), 2018.*

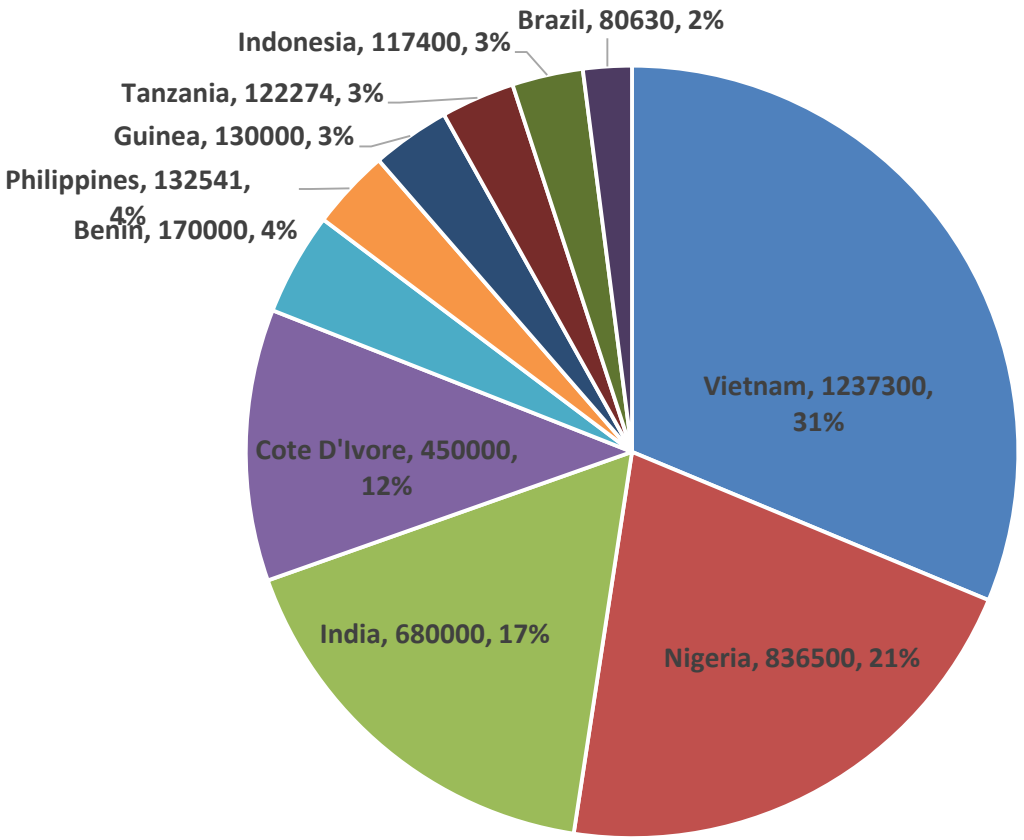
Cashew Plantation and CNSL Valorization: Global Value Chain



Cashew plantation: Coastal regions of Vietnam, Africa, India and Brazil.
CNSL value addition: USA, Europe, India, Vietnam and China.

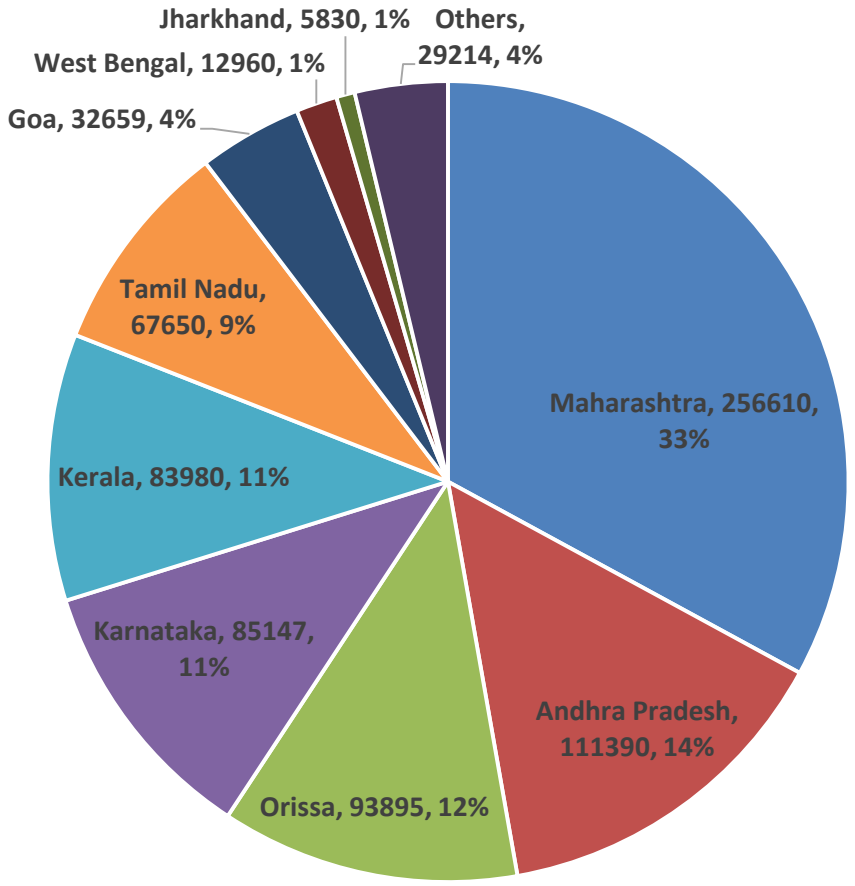
The Cashew Nut Production: A Global Perspective

Global



Total Production Global: 3956645 MT/a

India



Total Production India: 779335 MT/a

Cashew Processing Industry: Downstream Valorization

Cashew Nut

Kernel

Roasting

Natural CNSL

Technical grade CNSL

High Boilers

Cardanol

Specialty applications

WASTE TO WEALTH

Stages of value addition

First

Second

Third

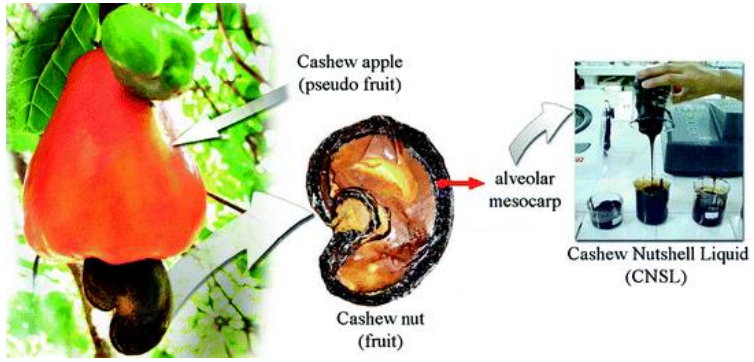
Fourth

More Players

Industry Ready

Increased Value

Cashew Nut Shell Liquid (CNSL): Extraction



Extraction of natural and technical CNSL from cashew nut shells

Mechanical Extraction

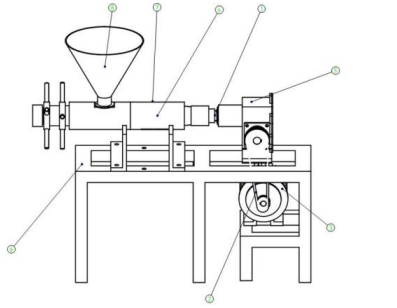
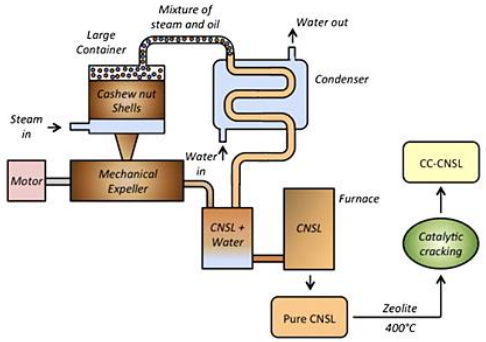


Fig. 1 Cashew Nut Shell Oil Extraction Machine

Legend: 1. Machine shaft, 2. Motor belt, 3. Motor, 4. Auger, 5. Reducer, 6. Frame, 7. Cylinder, 8. Hopper

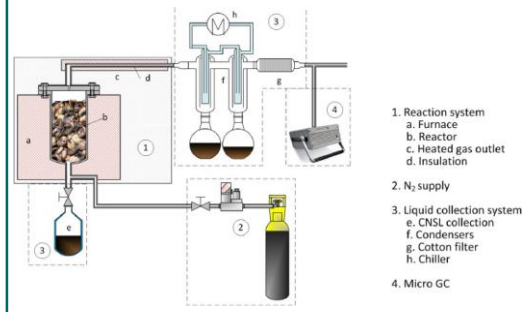
Thermal Extraction



Solvent Extraction

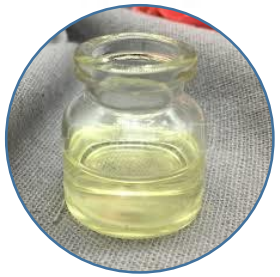
1. Static Solvent Extraction
2. Soxhlet Extraction
3. Ultrasonic Extraction
4. Supercritical CO_2 Extraction

Pyrolysis Method



The mechanical and thermal extractions are favorable and/or commercially practiced

CNSL Valorization: Industry Eco-system



Suppliers of CNSL Processing Ancillaries: Representative Examples

Technoforce Solutions (I) Pvt. Ltd. Nashik

TECHNOFORCE™ https://www.technoforce.net/

MEKONG VietNam

https://www.mktech.vn/cnsl-processing-technology/

Program Definition and Project Reports:

Entrepreneur India, Delhi

ei Entrepreneur India https://www.entrepreneurindia.co

NIIR Project Consultancy Services (NPCS), Delhi

npcs https://www.niir.org/

Kerala Cashew Board, kerala

KERALA CASHEW BOARD LTD An initiative of Government of Kerala https://keralacashewboard.com/

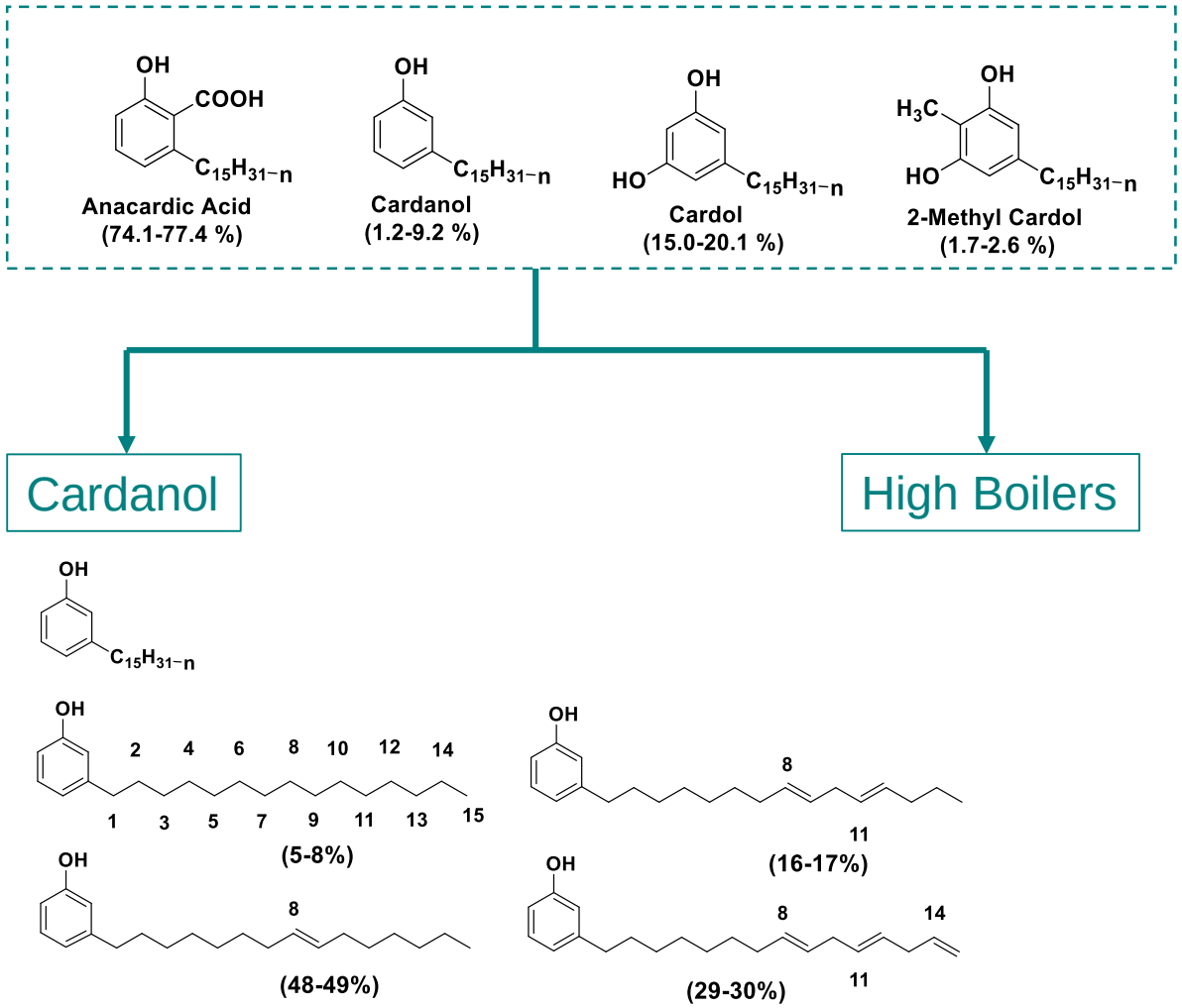
National Small Industries Corporation Limited, Delhi

एन एस आई सी NSIC https://www.nsic.co.in/

Small Industries Service Institute

(One in each state)

CNSL and Cardanol: Chemical Composition



Compound	Natural CNSL (wt%)	Technical CNSL (wt%)
Cardanol	1.2-9.2	74.1-77.4
Cardol	15.0-20.1	15.0-20.1
2-Methyl cardol	1.7-2.6	1.7-2.6
Anacardic acid	74.1-77.4	Trace amounts
Polymeric material		10

Reference: *G. Stadeler, Ann. Chem. Pharm., 63, 137-164 (**1847**).*

Cardanol: Opportunities for Replacing Petro-derived Phenols

Phenol	CAS No.	SVHC Rating
Phenol	108-95-2	
p-Tertiary Butyl Phenol	98-54-4	
p-Tertiary Octyl Phenol	140-66-9	
Bisphenol A	80-05-7	
Resorcinol	108-46-3	
Nonyl Phenol	84852-15-3	
m-cresol	108-39-4	
o-cresol	95-48-7	
p-cresol	106-44-5	
Bisphenol F	620-92-8	
Cardanol	37330-39-5	

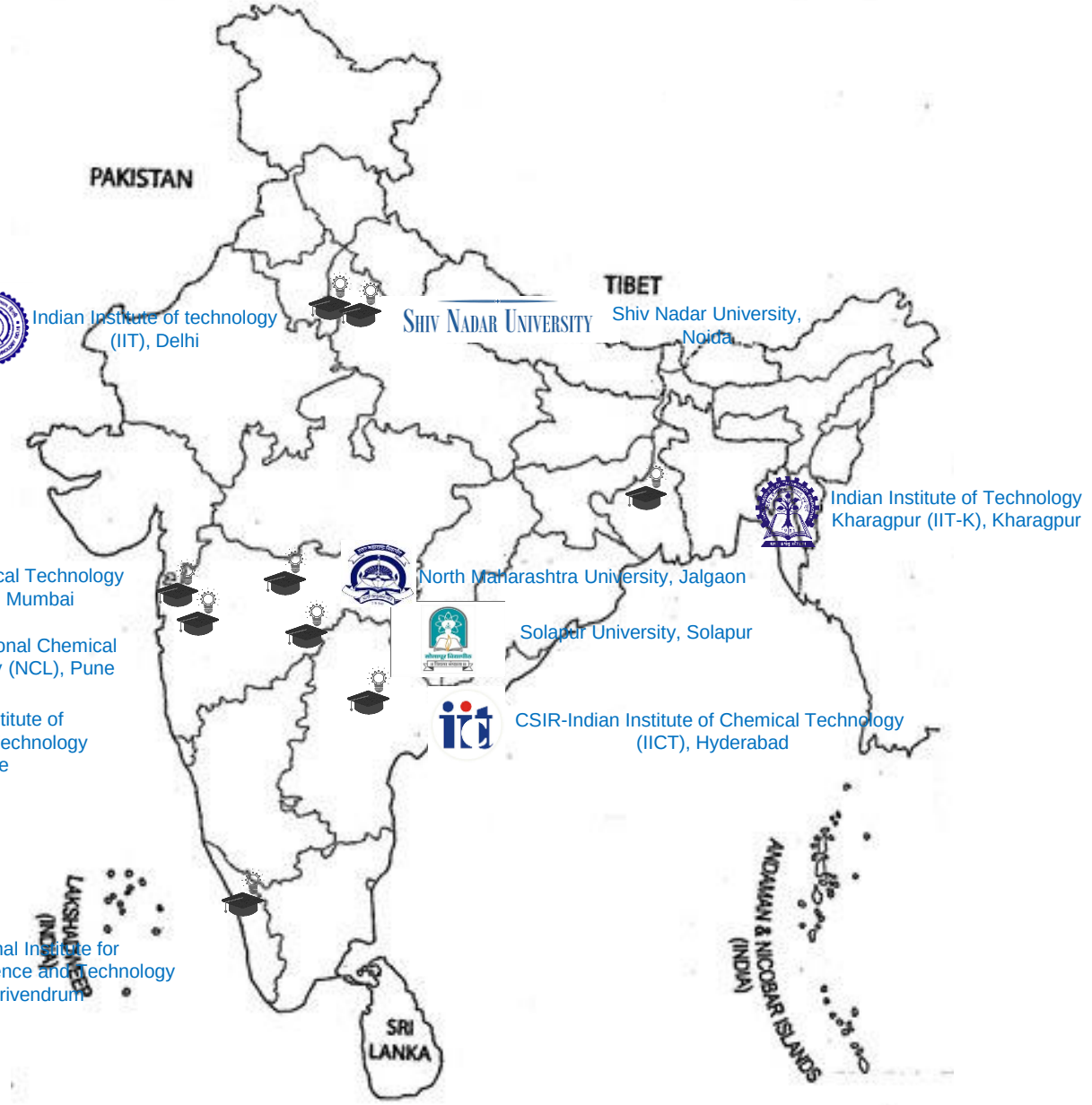
SVHC: Substances of very high concern

https://reachonline.eu/reach/en/title-vii-chapter-1-article-59.html

CNSL Valorization: India's Contributions

Dr. N. D. Ghatge

Dr. C. K. S. Pillai



Indian Institute of technology (IIT), Delhi

Shiv Nadar University, Noida

Indian Institute of Technology Kharagpur (IIT-K), Kharagpur

North Maharashtra University, Jalgaon

Solapur University, Solapur

CSIR-Indian Institute of Chemical Technology (IICT), Hyderabad

Institute of Chemical Technology ICT (UDCT), Mumbai

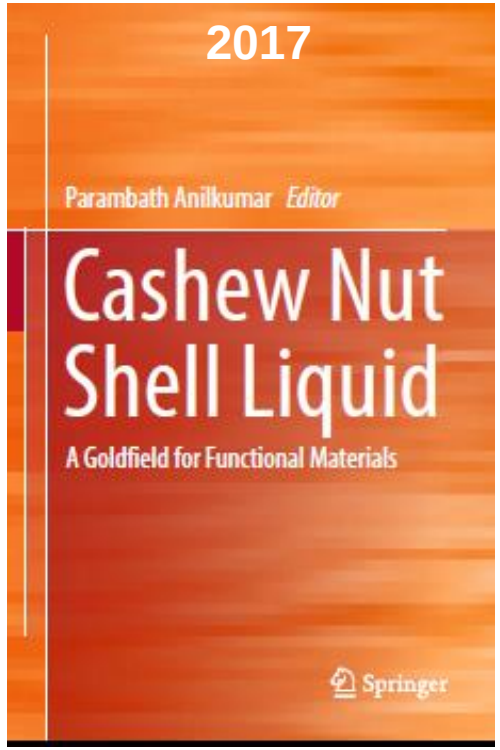
CSIR-National Chemical Laboratory (NCL), Pune

Indian Institute of Science Education and Research (IISER), Pune

Defence Institute of Advanced Technology (DIAT), Pune

Vikram Sarabhai Space Centre (VSSC), Trivandrum

CSIR – National Institute for Interdisciplinary Science and Technology (NIIST), Trivendrum



Portfolio	No.
Publications	3000
Patents	2000
Citations	30000

CNSL Valorization: Major Indian Industries

ADARSH INDUSTRIAL CHEMICALS

ADMARK POLYCOATS PVT. LTD.

Paladin Paints & Chemicals Pvt. Ltd.

SATHYASHREE INDUSTRIES

SCCPL

K2p Chemicals
Andheri West, Mumbai, Maharashtra

CASHEW CHEM INDIA

Golden Cashew Products Pvt.Ltd.

RK CASHEW

NOVOSIS GREEN TECHNOLOGIES

South Indian chemicals

SAI CASHEWS
Natural & Quality Nuts

झांट्ये आंबो Zantye Agro

GOLDEN AGRO

RRC
Rishabh Resins & Chemicals

NAYAKEM
Since 1970

Majority of Indian players cater to commodity applications.

CNSL Valorization: Major Foreign Industries

https://www.cardolite.com/

https://www.carboline.com/

http://palmerint.com/

http://www.senesel.pl/en

https://cardanol.vn/

Zhejiang Wansheng Co. ltd.

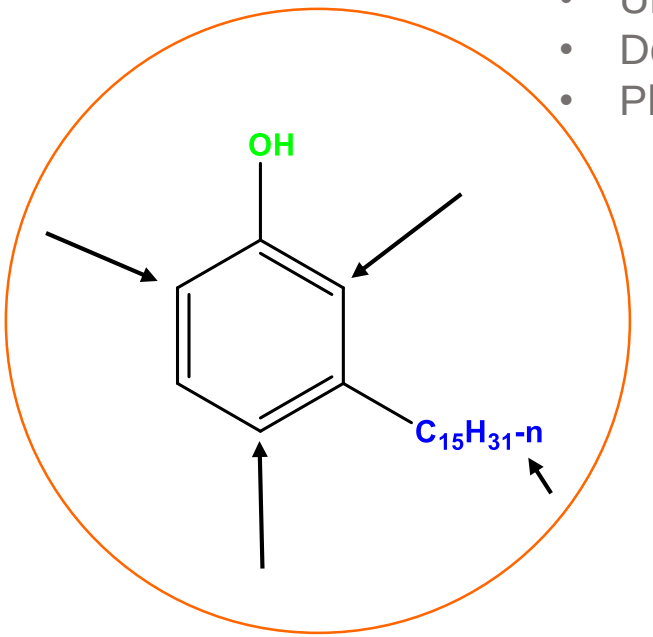
http://www.ws-chem.com/en/index.aspx

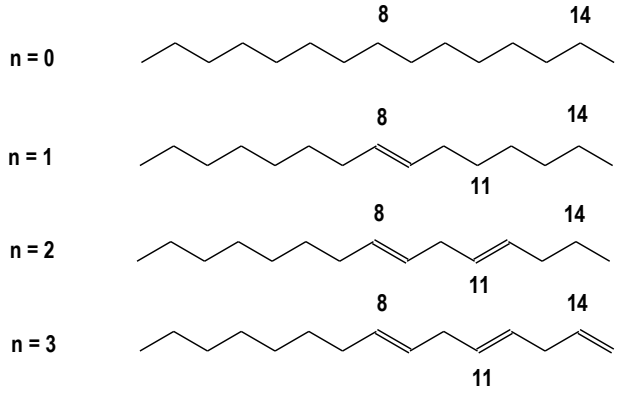
http://www.sdhaobobio.com/shown.asp?id=244

Cardanol: A Versatile Building Block

Reactions at the aromatic ring:

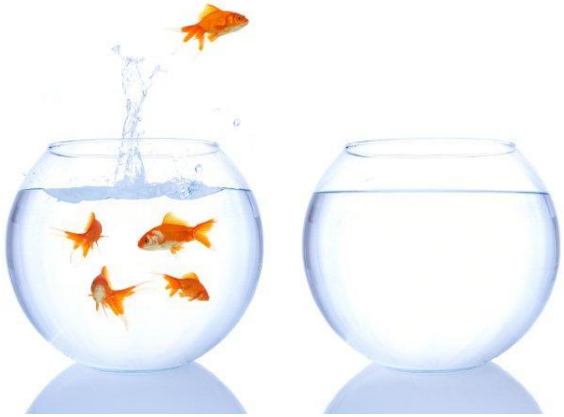
- **Aromatic electrophilic substitution reactions**
  (halogenation, nitration, sulphonation)
- Aromatic condensation/Mannich chemistry
- **Enzymatic coupling**
- Ring hydrogenation





Reactions at OH group:

- **Alkylation**
- Acylation
- Ullmann etherification
- Dehydration
- Phosphorylation

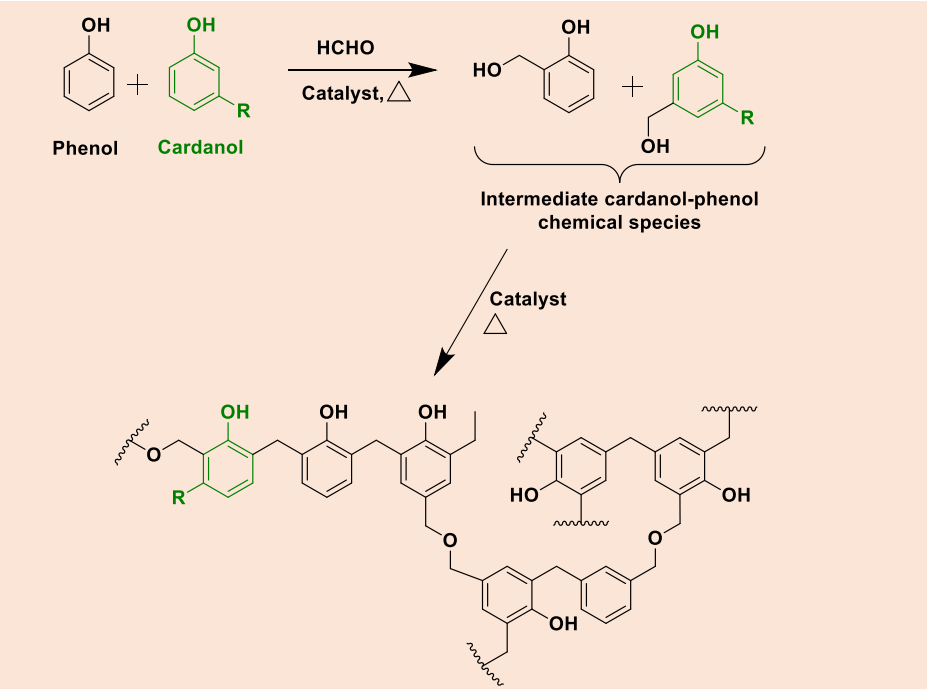


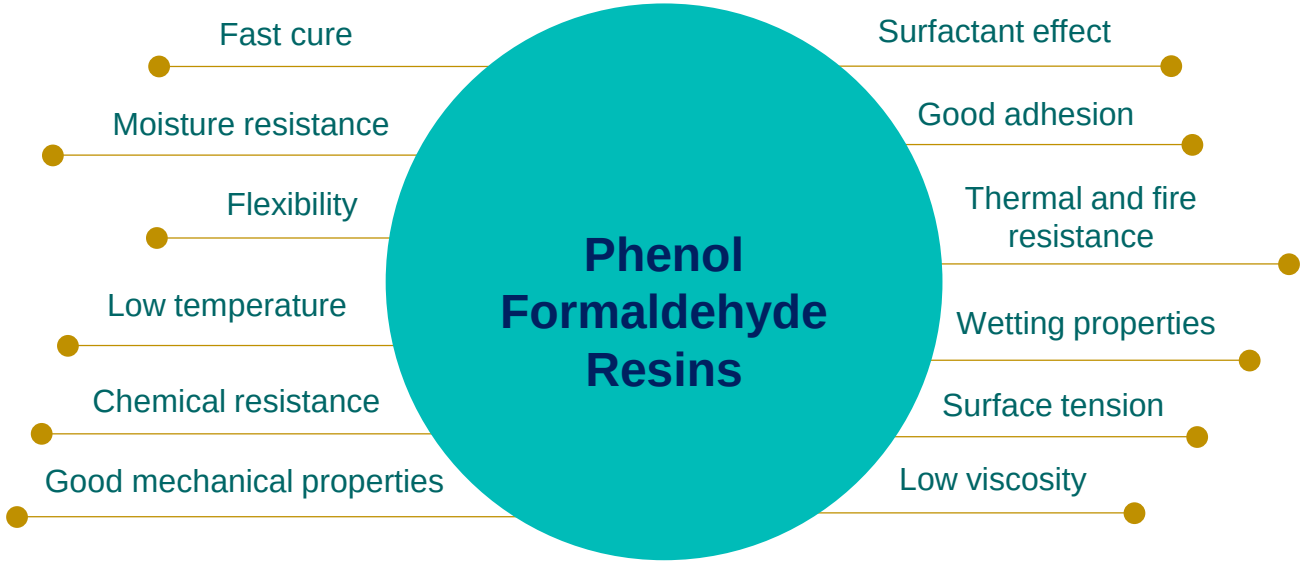
Differentiated products
Enhanced Performance

Reactions at double bonds in the side chain:

- Hydrogenation
- Bromine addition
- **Epoxidation**
- Hydrosilylation
- Hydroboration
- Phenolation
- Oxidative polymerization/Oligomerization
- Ozonolysis
- Metathesis
- Thiol-ene reaction

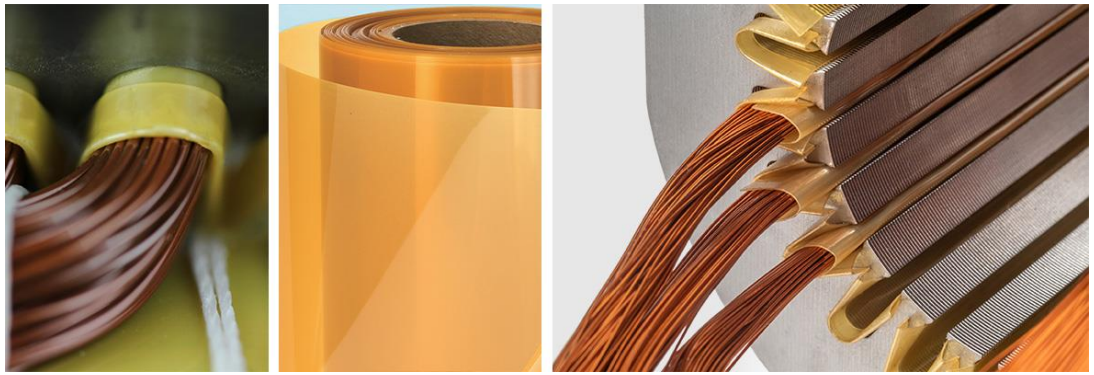
CNSL-based Phenol Formaldehyde Resins





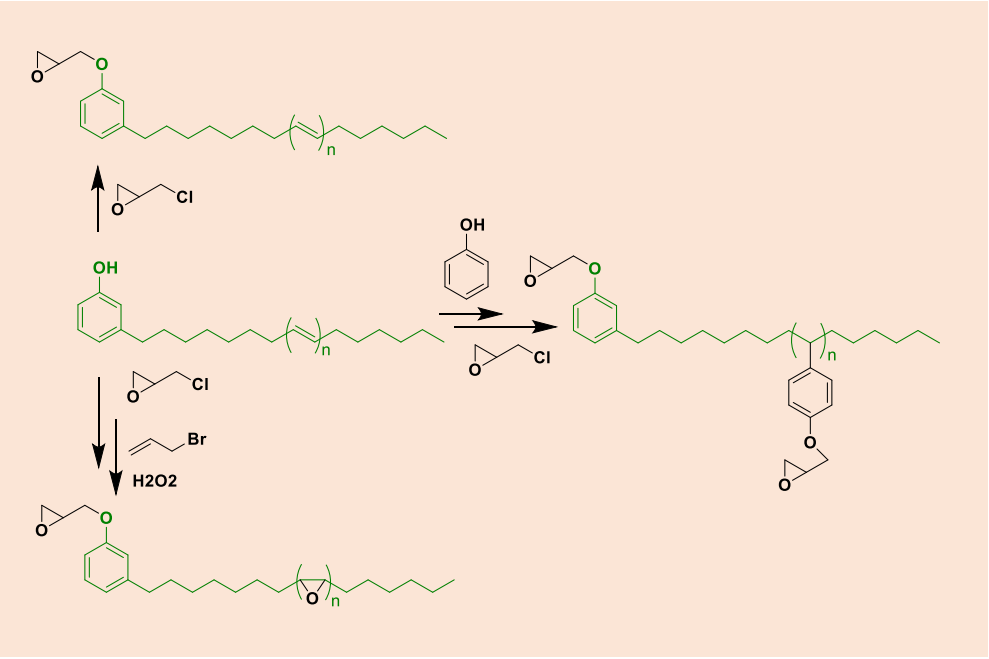
Composite

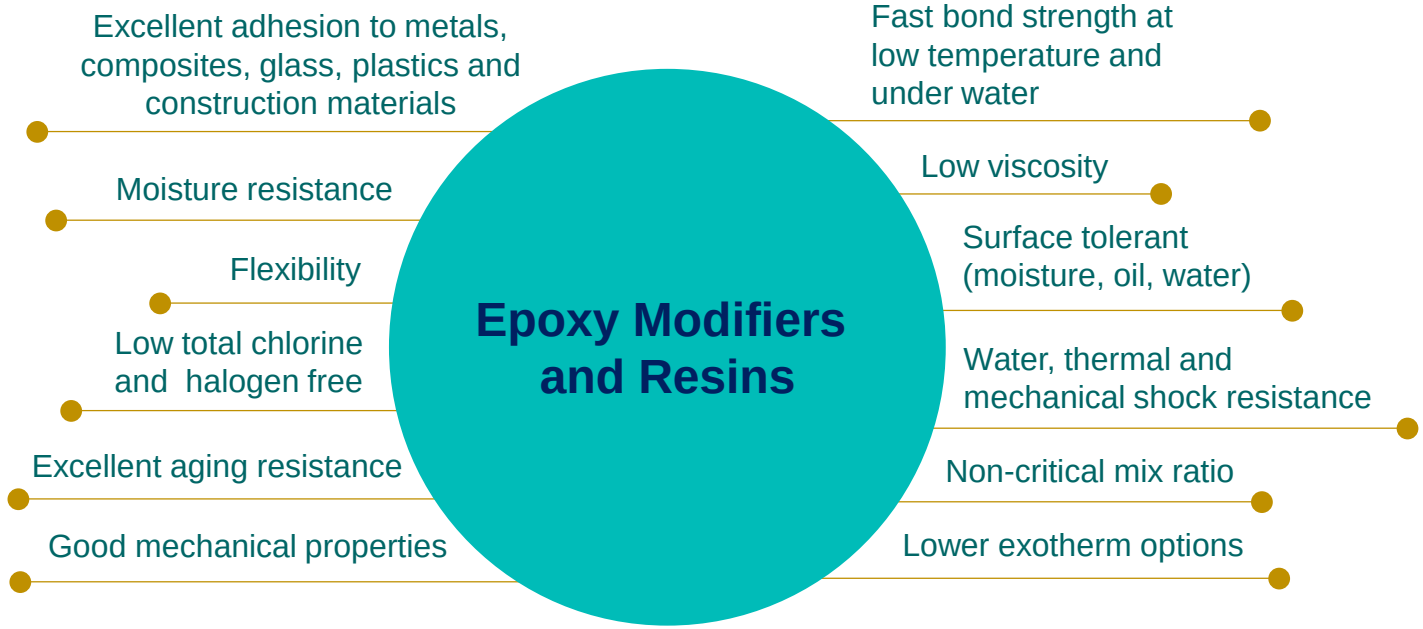
Electrical Insulation



Laminates

CNSL-based Epoxy Diluents, Modifiers and Resins

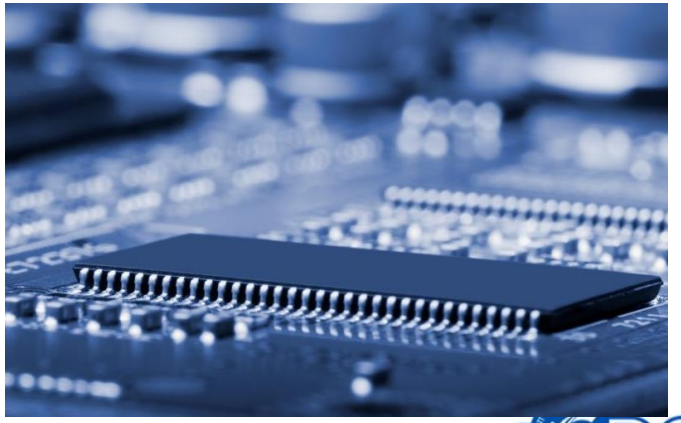




Industrial and Transportation

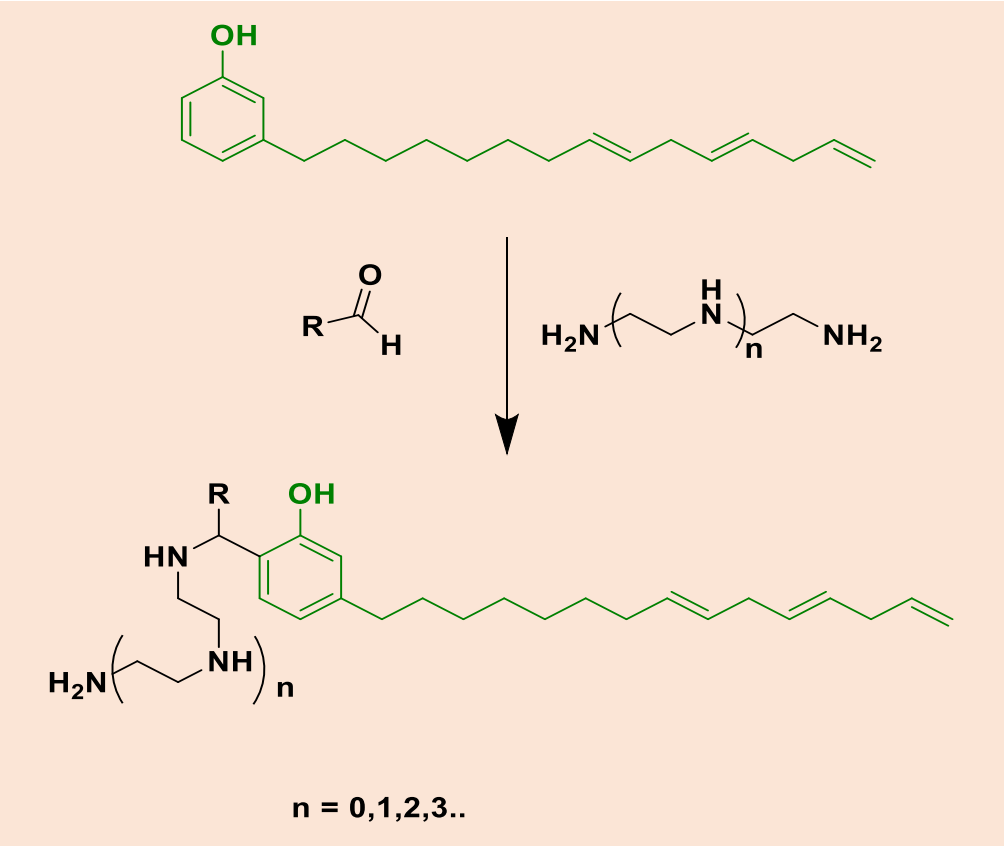
Building and Construction Adhesives

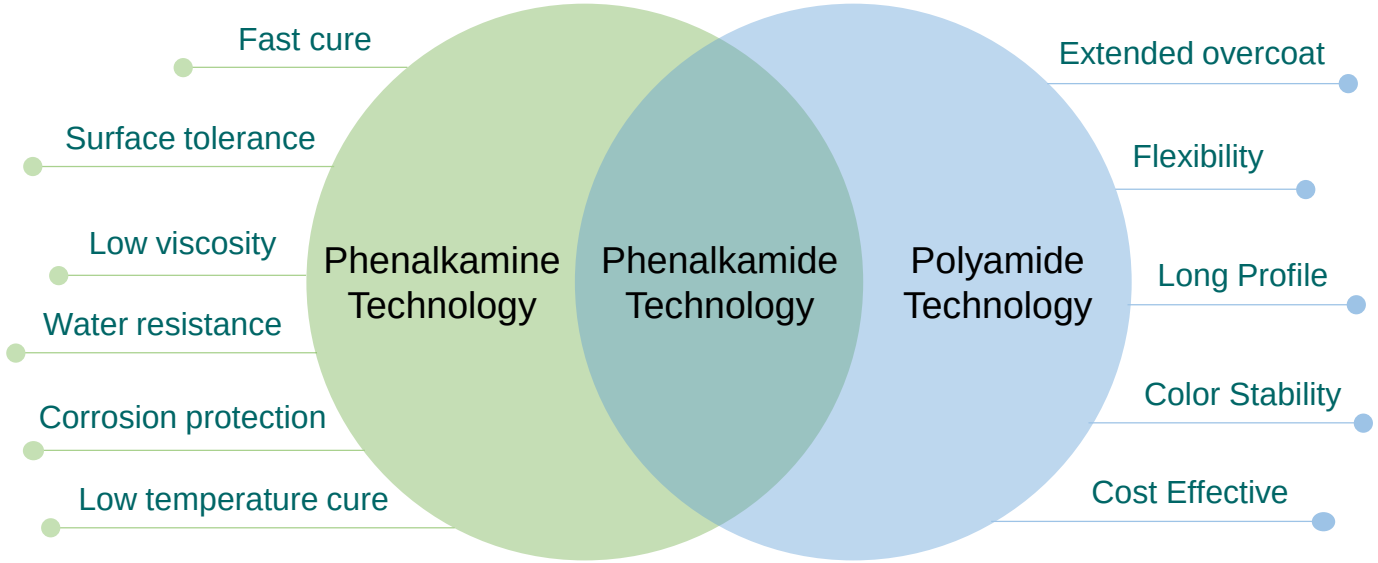
Electronics Adhesives



CNSL-based Epoxy Curing Agents

Phenalkamines are reactive, Mannich- based amine (Phenalkamine) hardener.





A new category of renewable epoxy curing agents designed to provide coating formulators with the benefits of both polyamides and phenalkamines in **ONE PRODUCT**

Marine Coating

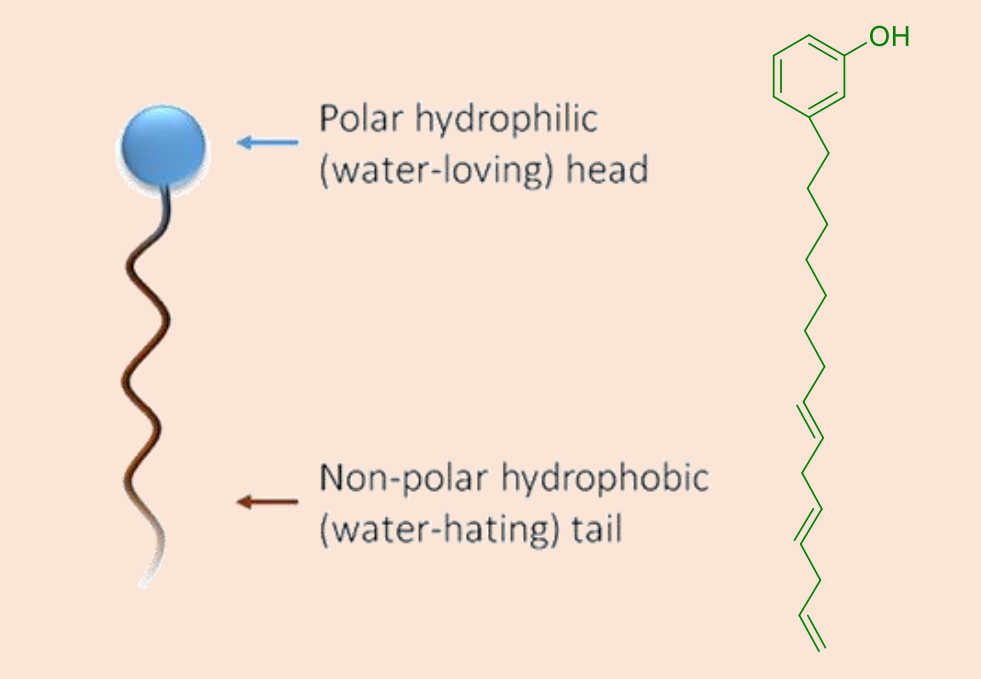
Industrial Coating

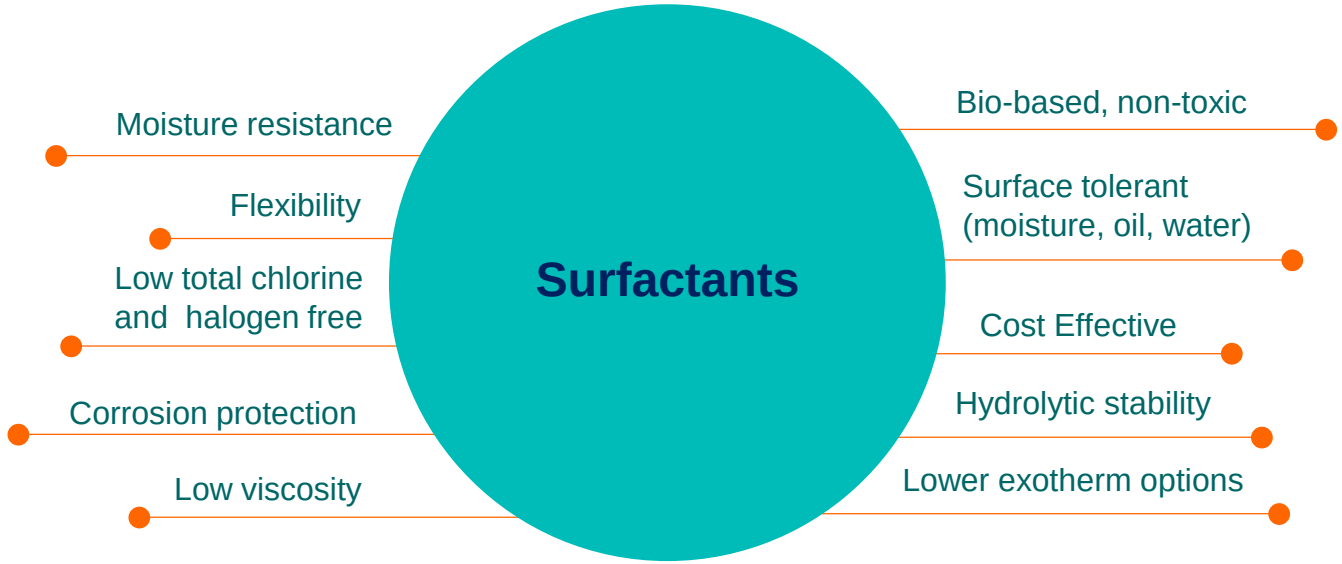
Protective Coating

Advantages:

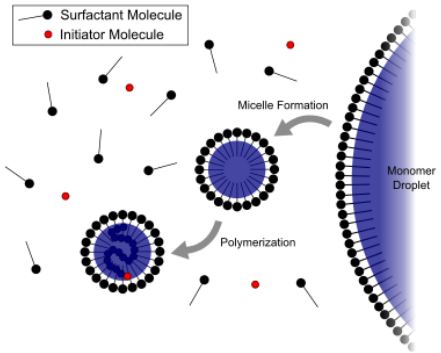
1. W/w replacement for polyamides.
2. Short re-coatable time, **time saving**.
3. All season curing agent, **less inventory**

CNSL-based Surfactants





Emulsion Polymerization

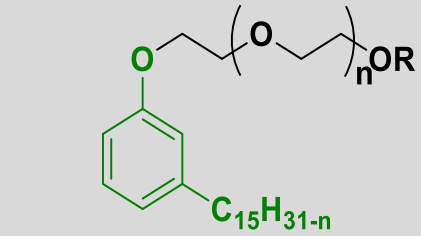


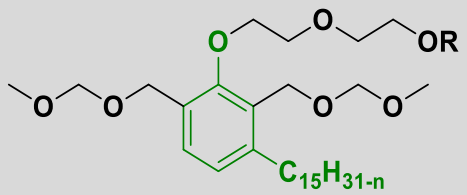
Personal Care

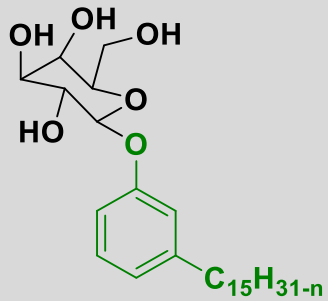
Petroleum Demulsifiers and Dispersants

CNSL-based Representative Surfactants

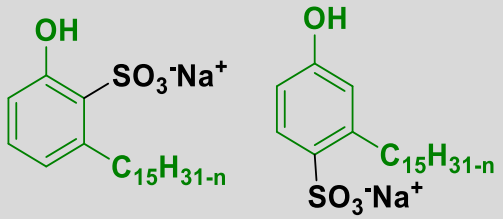
Non ionic

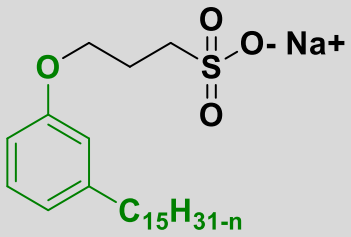






Anionic





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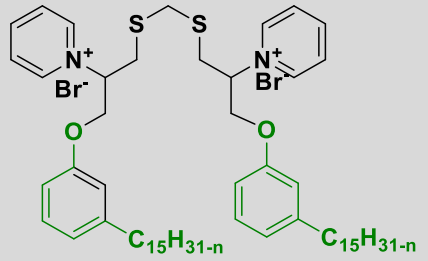
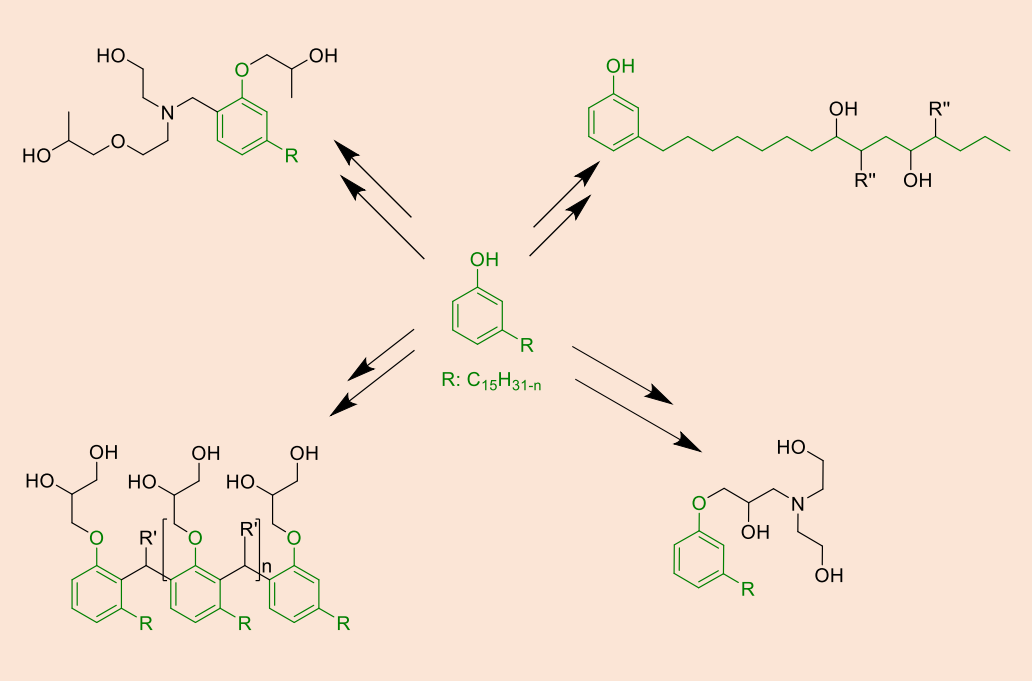
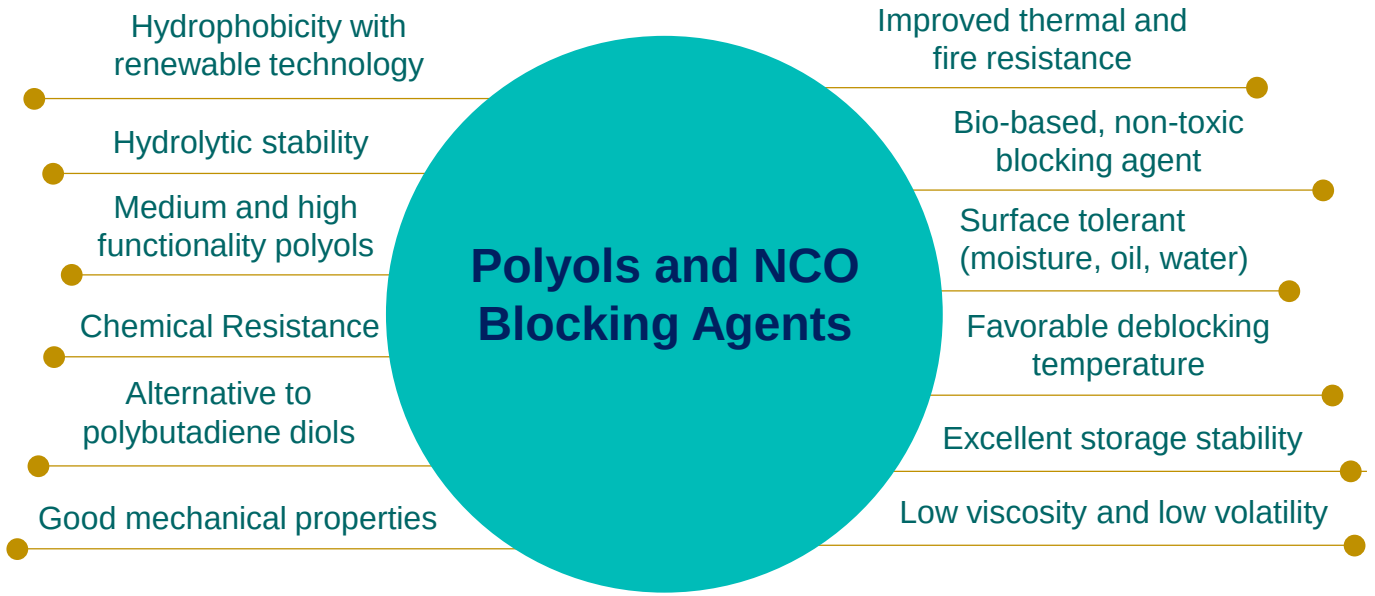


CNSL-based Polyols and NCO Blocking Agents



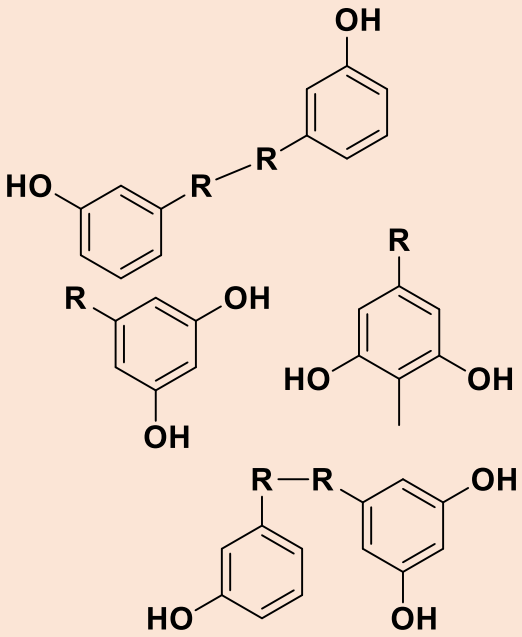


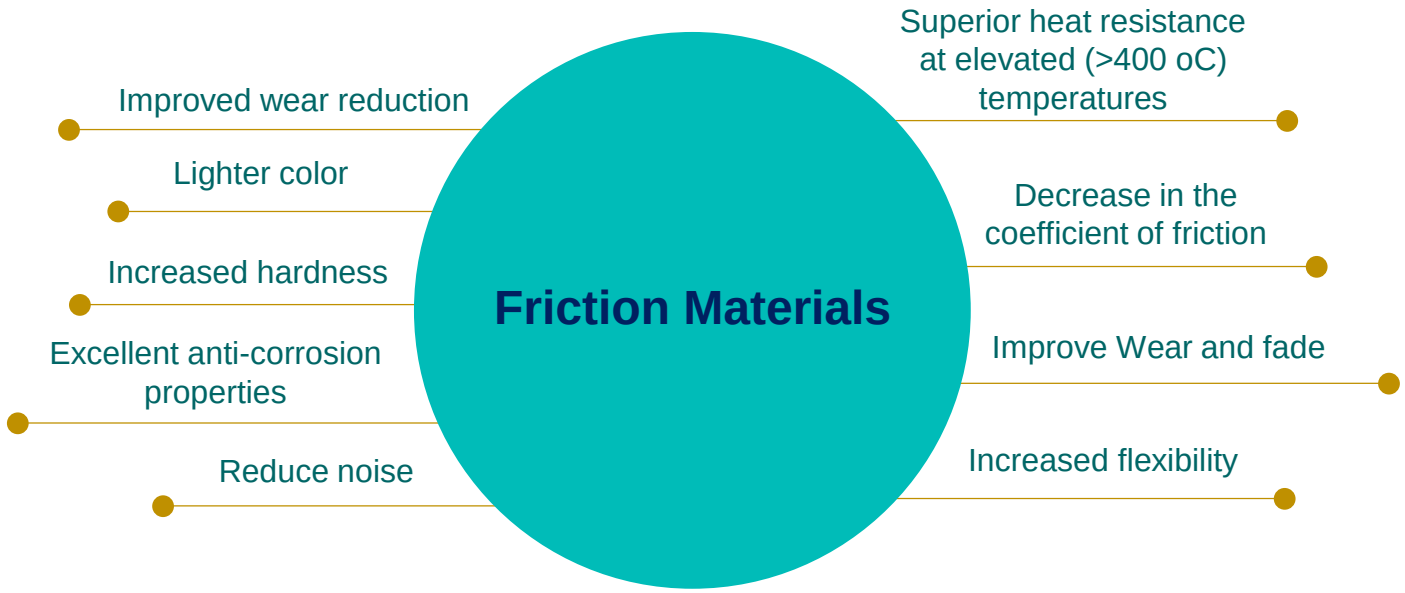
1 Pot, 2 Pot Epoxy Adhesive

Rigid PU Foams

1K PU Hot Melt Adhesive

CNSL-based Friction Materials



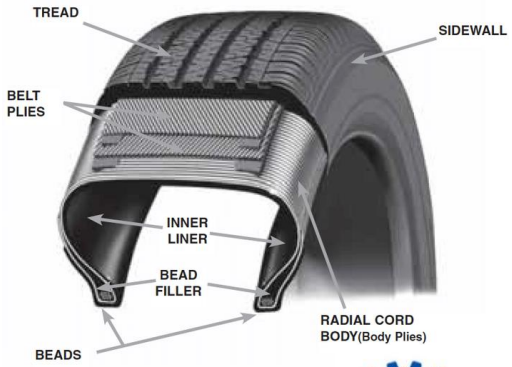


Automotive Break Industry

- Brake linings
- Disc pads
- Blocks
- Belts together
- Rail break shoes
- Binder resins

Train

Tire bead Filler

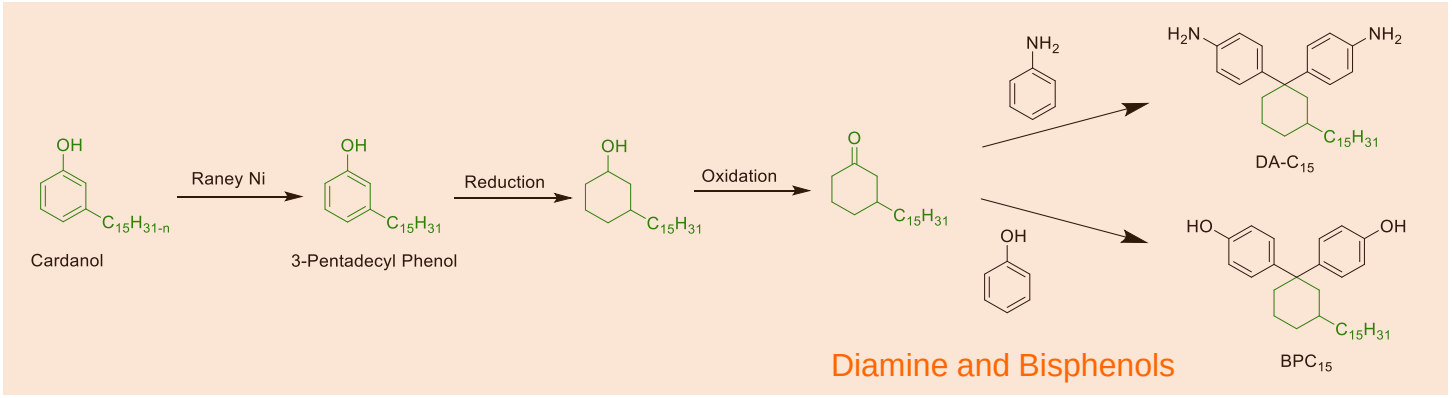


CNSL Valorization: Our Contributions from PSE, CSIR-NCL

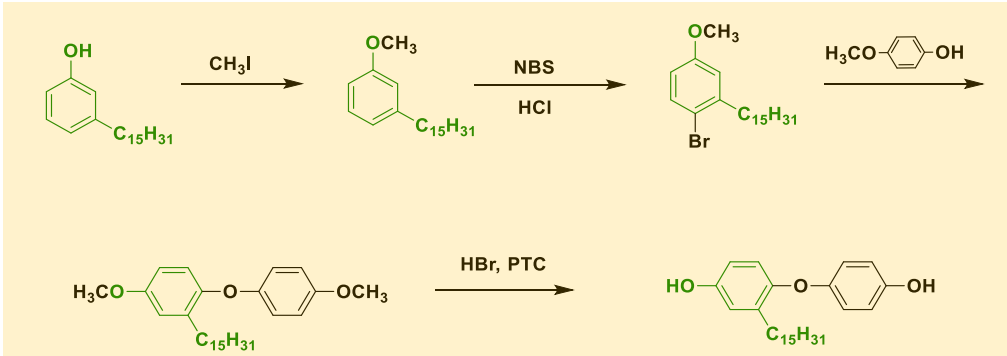
…The Team

- Simple organic transformations
- Scalable processes (demonstrated up to Kg scale)
- Entry into high end/specialty applications
- IP creation for CSIR
- Industry collaborations
- Creation of skilled human resource to address renewability challenges
- Potential for job creation at India.

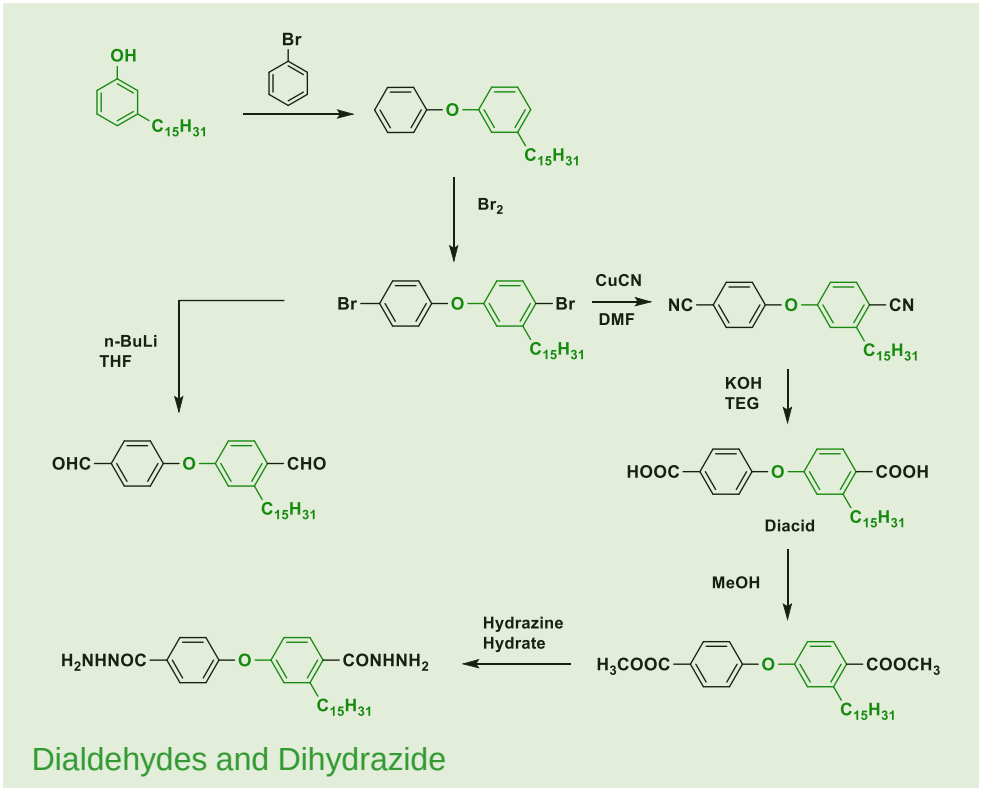
Functionalization of CNSL: Art of Possible



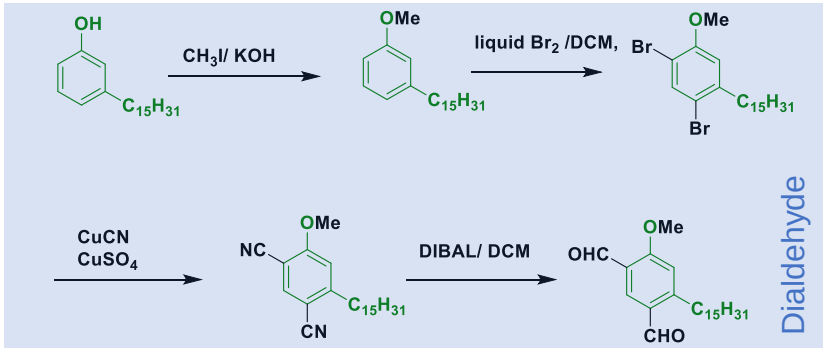
Diamine and Bisphenols



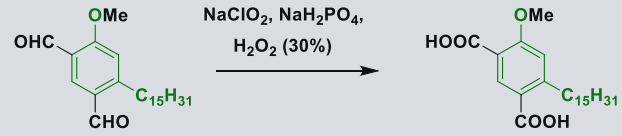
Bisphenols with ether linkage



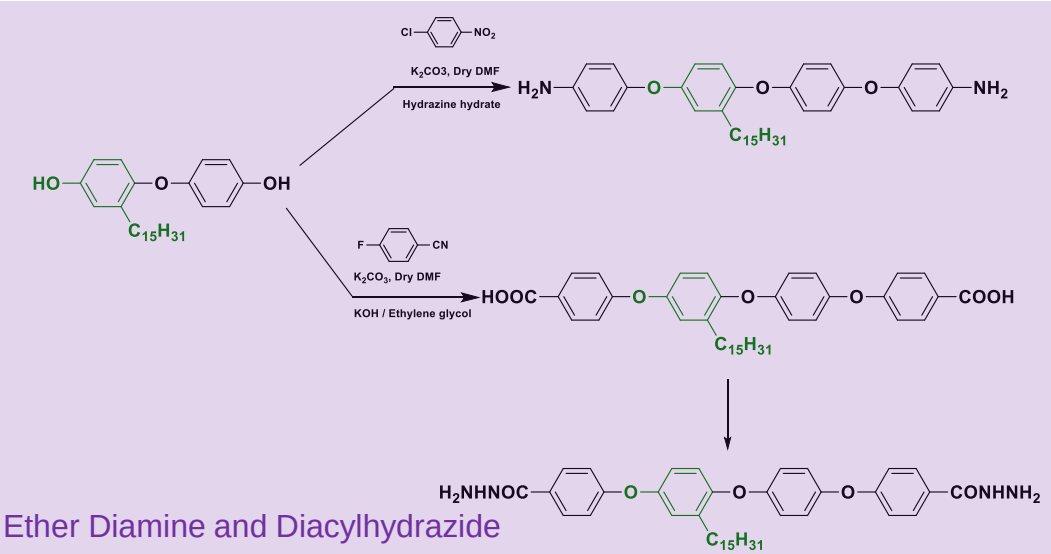
Dialdehydes and Dihydrazide



Dialdehyde



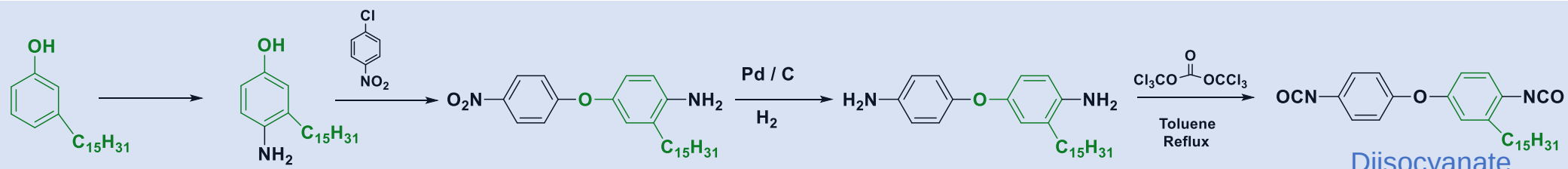
Diacid

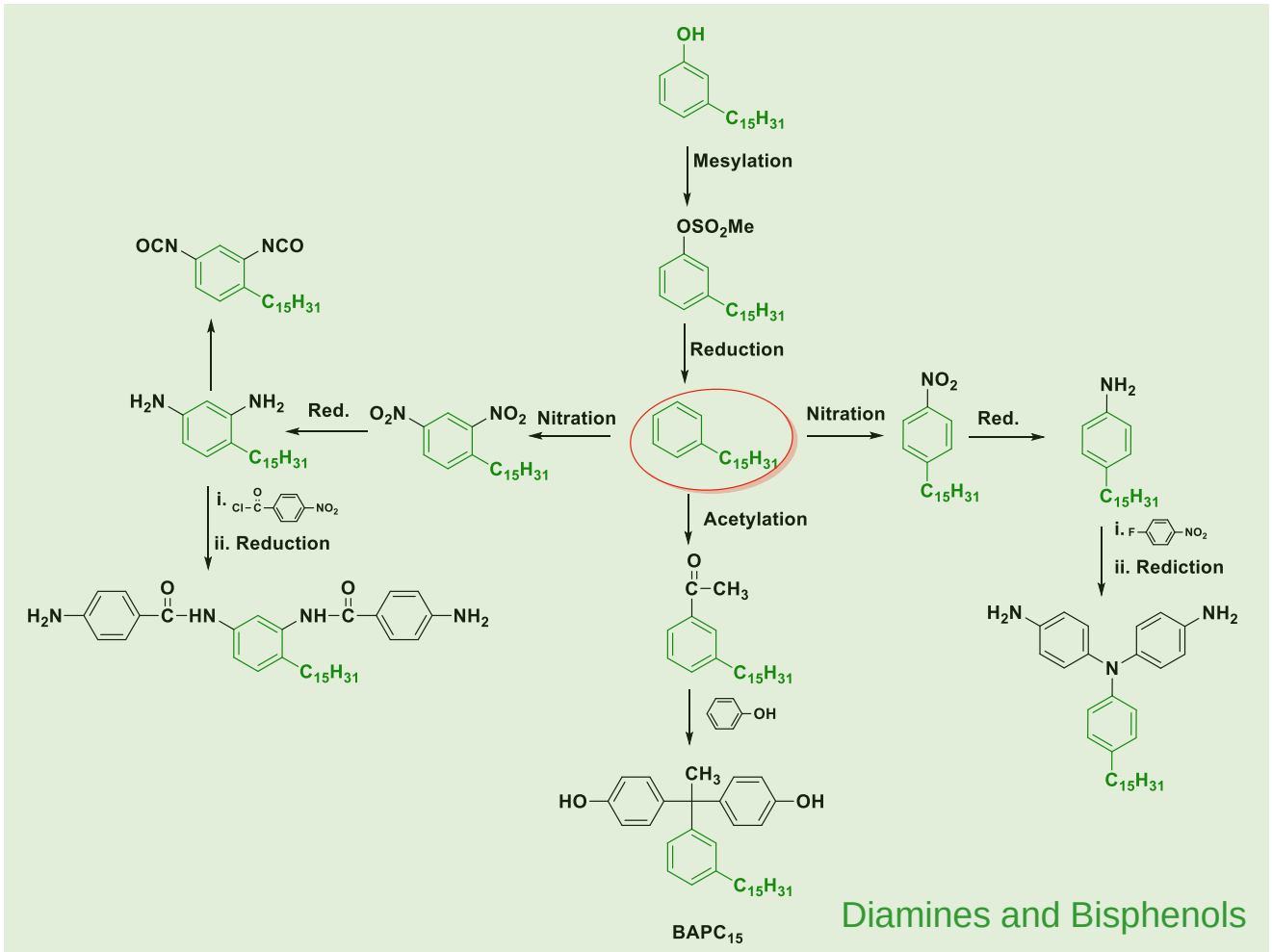


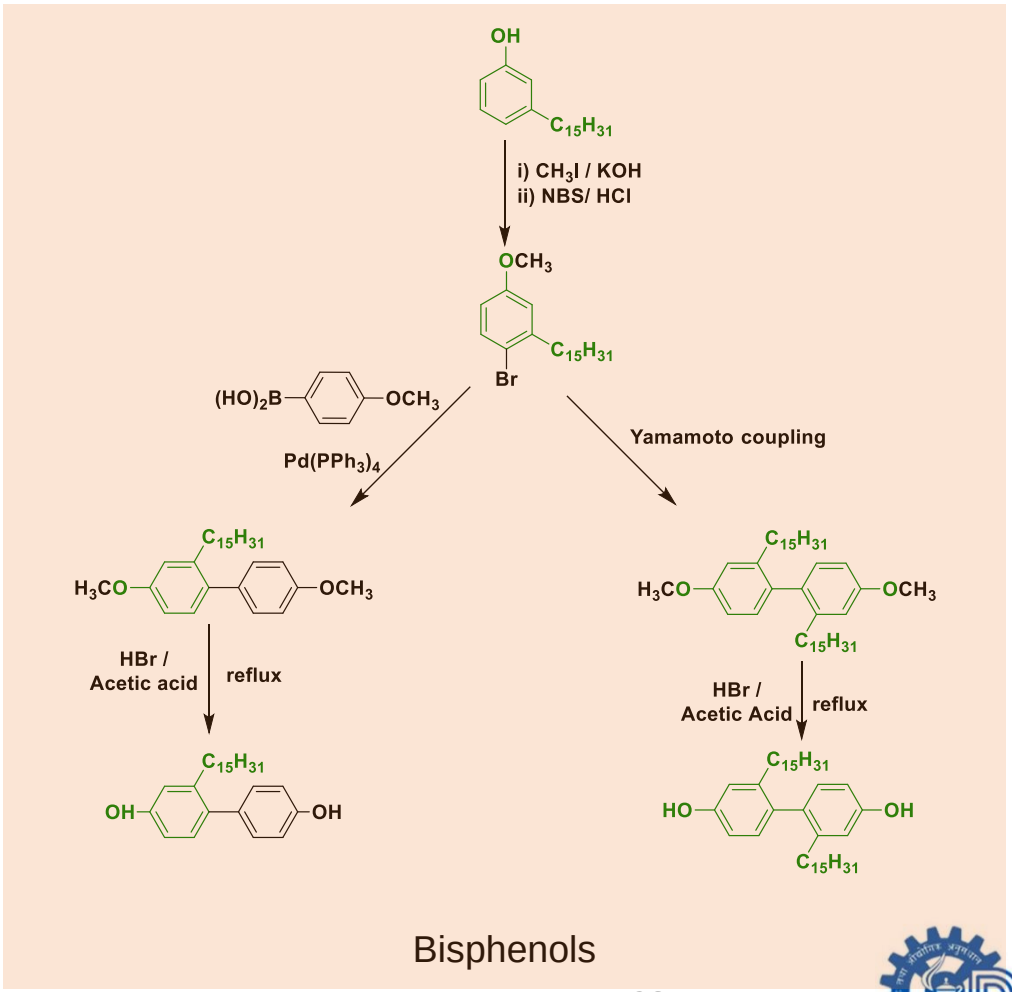
Ether Diamine and Diacylhydrazide

29 October 2020

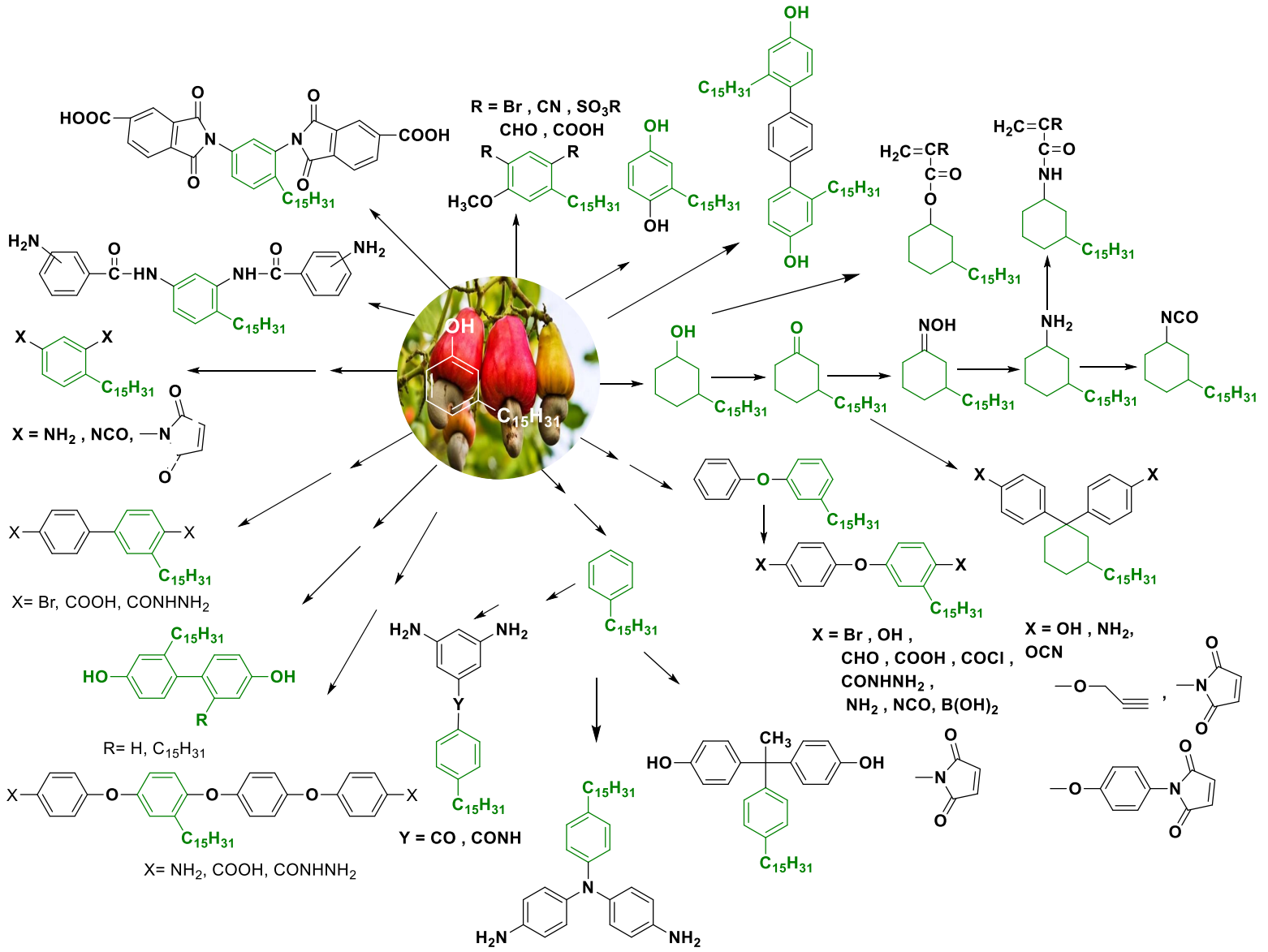
Functionalization of CNSL: Art of Possible







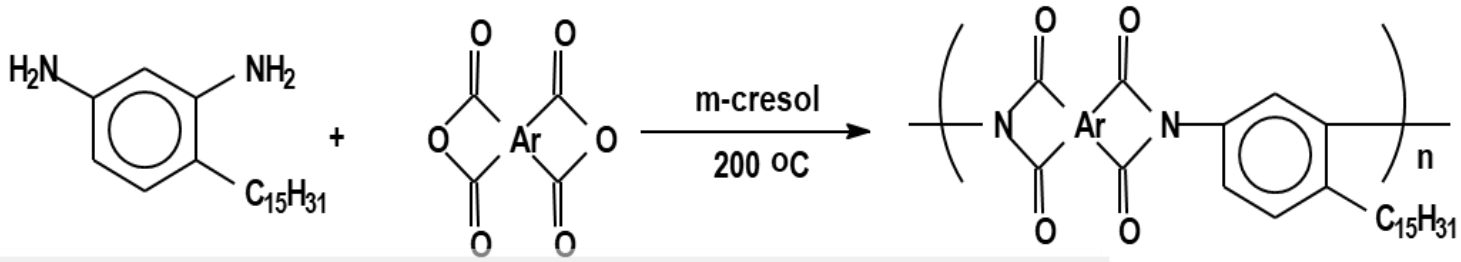
CNSL-based Bio-platform: Our Group's Contributions

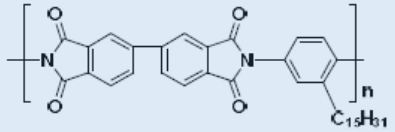
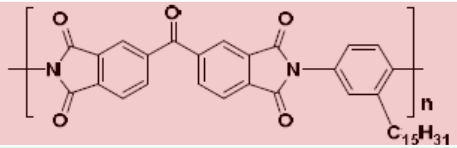
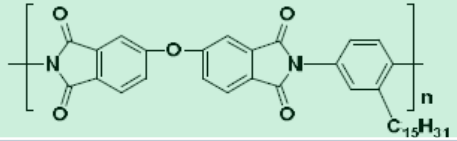
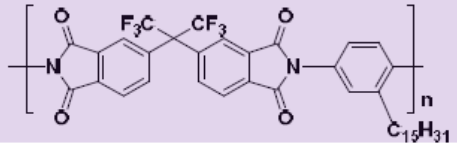


A Wide Range of Value Added Chemicals and Difunctional Monomers Synthesized.

Polym. Chem., 2014, 5, 3142-3162

CNSL: Polyimides



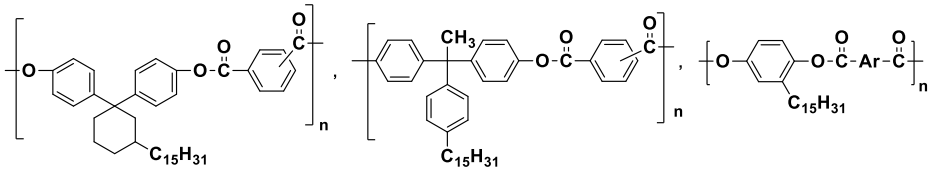
Polyimide	Repeating Unit	η_{inh}[a] (dL/g)	GPC[b] M_n	GPC[b] M_w	GPC[b] M_w/M_n	Thermal Properties T_g[c]	Thermal Properties T_{10}
PI-1		0.67	52,200	1,19,000	2.2	206 (320)[d]	475
PI-2		0.49	14,700	28,100	1.9	176 (320)[d]	470
PI-3		0.56	38,200	76,000	2.0	159 (305)[d]	480
PI-4		0.33	48,700	95,000	1.9	158 (297)[d]	480

Polyimide Film

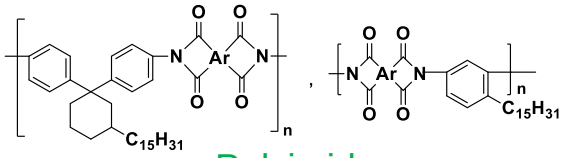
[a] Measured at a concentration of 0.5 g/dL at 30 ± 0.1 °C in $CHCl_3$.
[b] Determined from gel permeation chromatography (mobile phase: chloroform; calibration: polystyrene standards).
All Polyimides were soluble in common organic solvents
[c] Glass transition temperature (Tg) measured on DSC at a heating rate of 10°C/min in N_2.
[d] Values in the bracket are T_g values of parent polyimide based on *m*-phenylene diamine and corresponding dianhydride

Processable polyimides with acceptable thermal properties

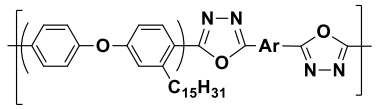
CNSL: High Performance Polymers (Thermoplastics)



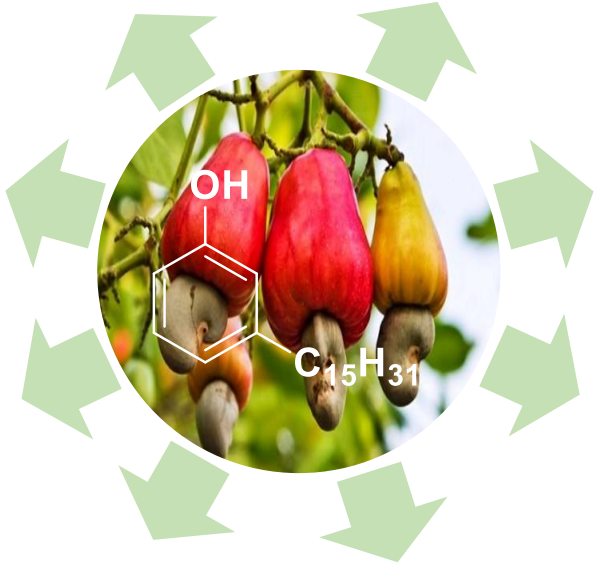
Polyesters

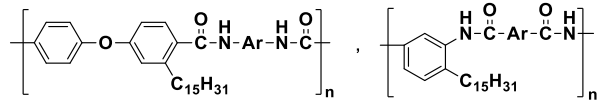


Polyimides

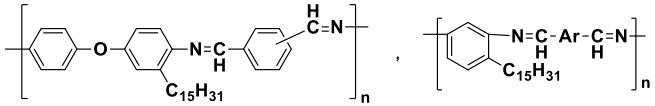


Poly(oxadiazole)s

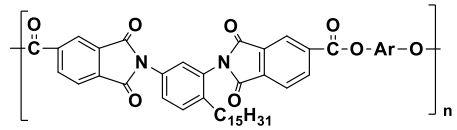




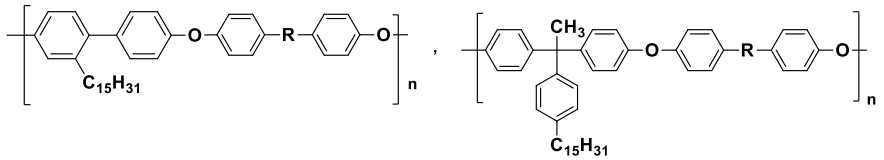
Polyamides



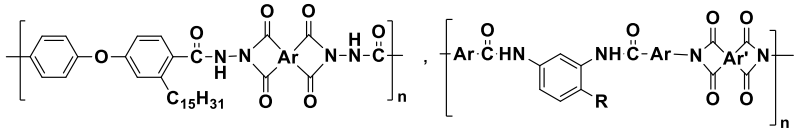
Poly(azomethine)s



Poly(esterimide)s



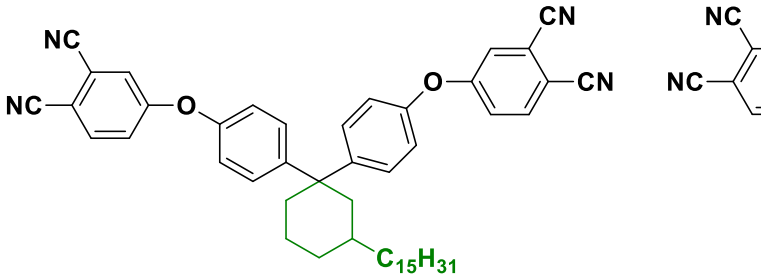
Poly(arylene ether)s

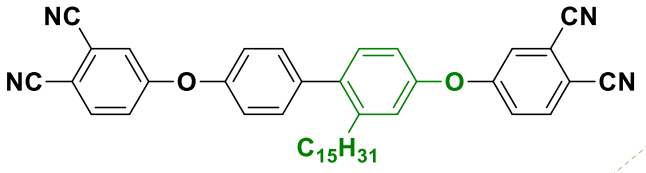


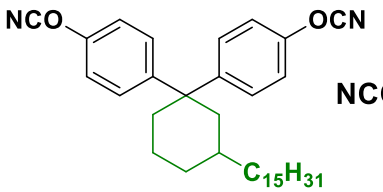
Poly(amideimide)s

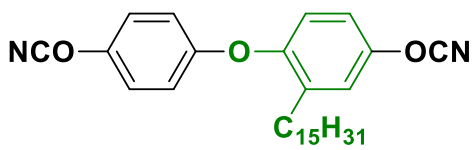
The processability was improved due to presence of pendent aliphatic side chains.

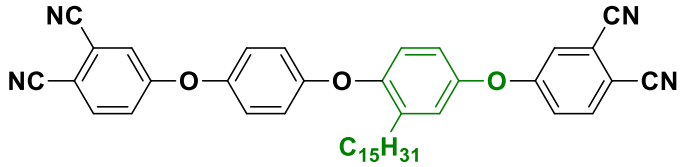
CNSL: Thermoset Resins





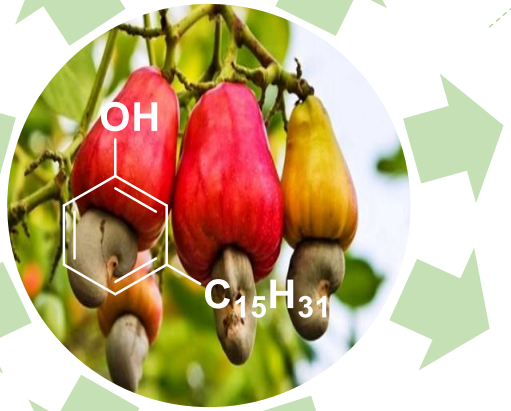






Bis-phthalonitriles

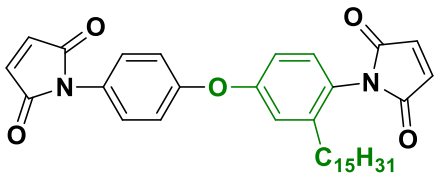
Cyanate Ester

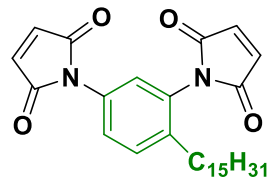


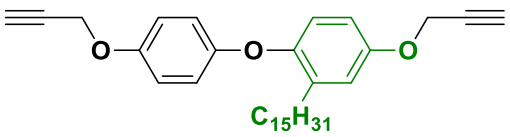
Bispropargyl Ethers

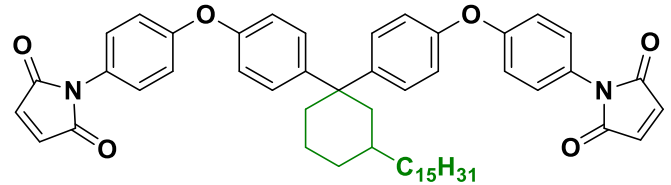
Bis-maleimides

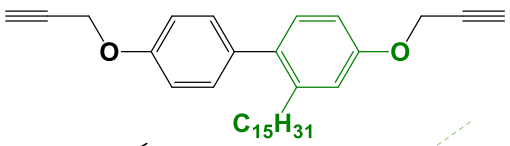
Epoxy Resins

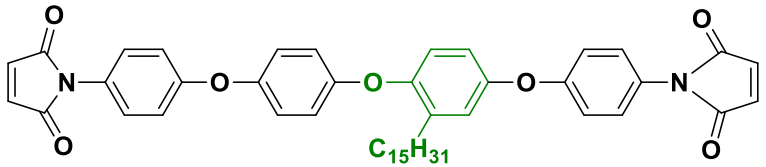


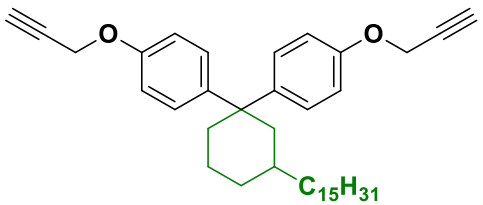


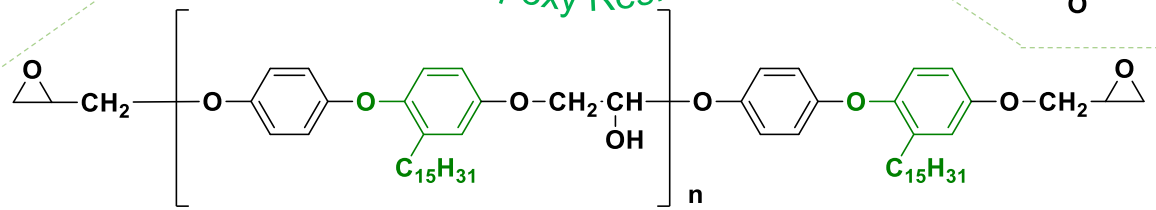


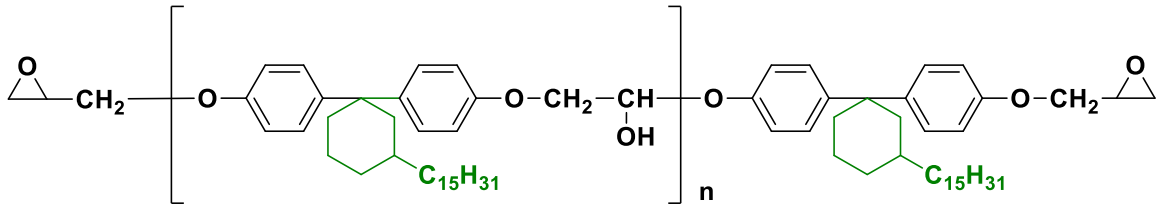








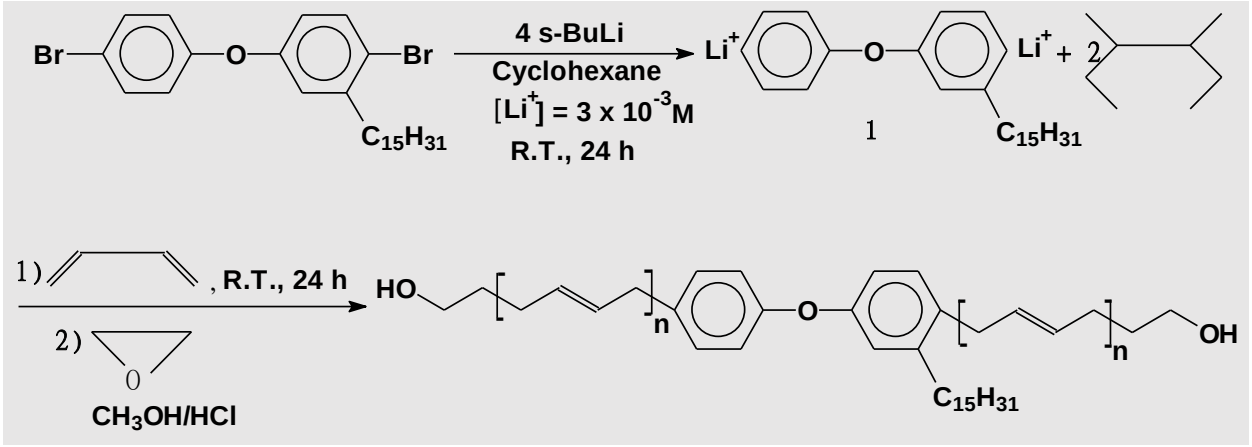




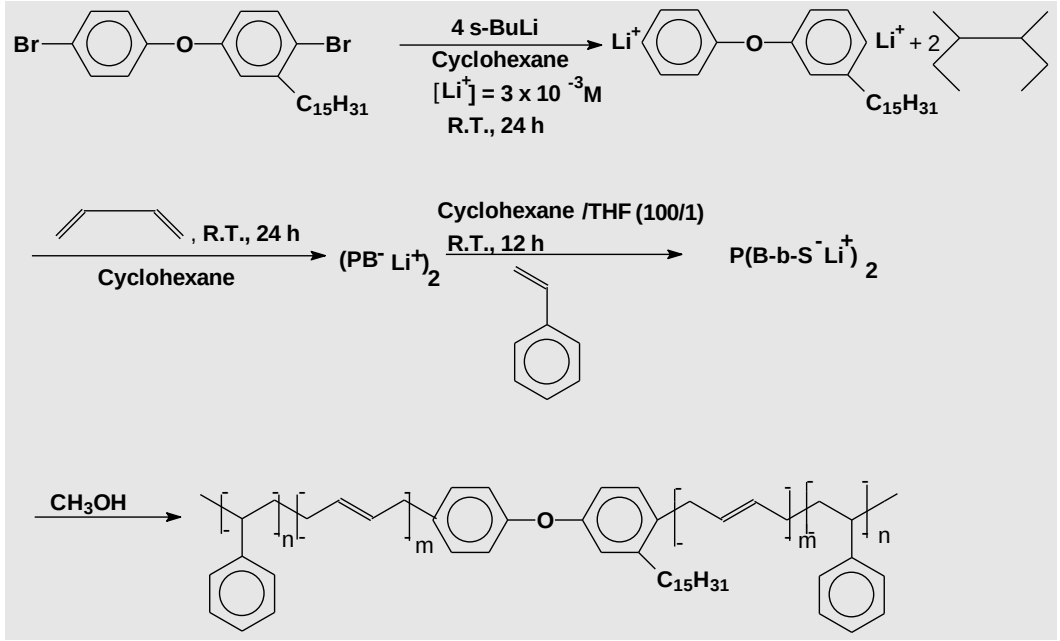
CNSL: Elastomers

The first example of bio-based and hydrocarbon-soluble dilithium initiator for anionic polymerization

α,ω-Dihydroxyl Polybutadiene Telechelics



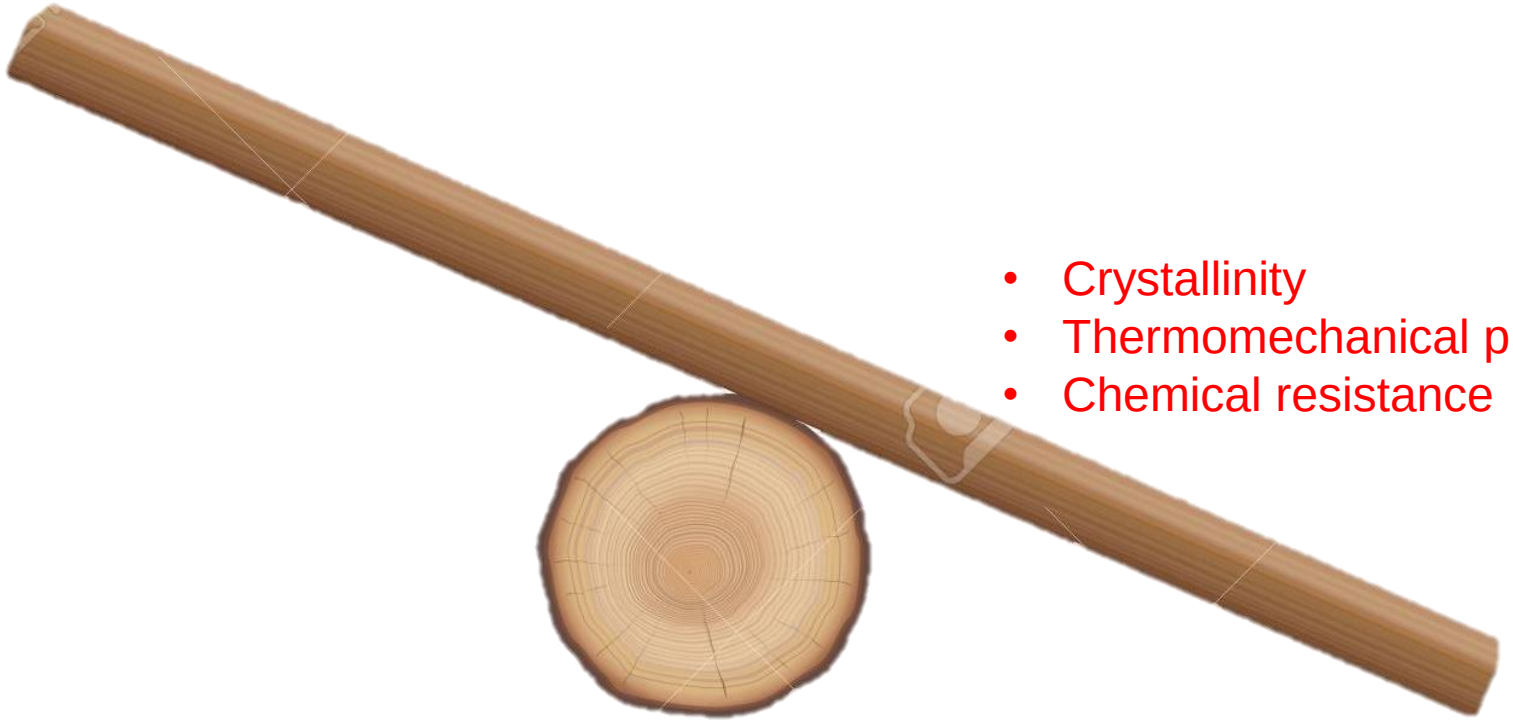
Synthesis of SBS Triblock Copolymers



Access to controlled macromolecular architectures and elastomeric performance

CNSL/Cardanol: Salient Conclusions and Outcome of Our Work

- Solubility in (common) organic solvents
- Lower Moisture uptake
- Ductility/Impact
- Tg
- Lower Melting point of thermoset monomers



- Crystallinity
- Thermomechanical properties
- Chemical resistance

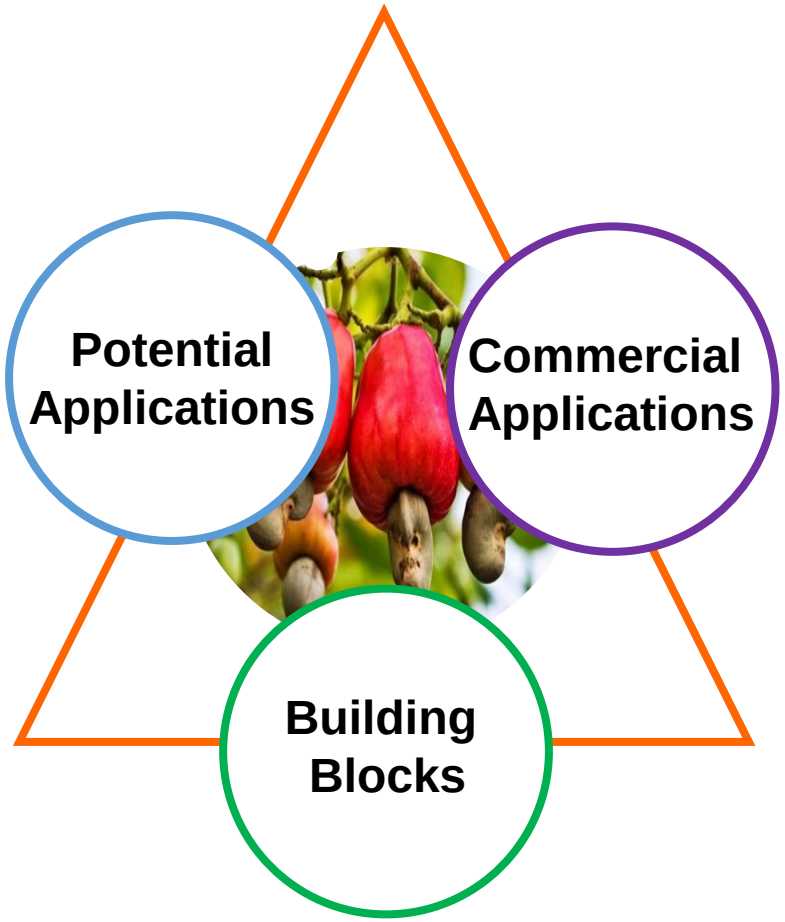
- Pentadecyl side chain acts as a packing distruptive group (bound plasticizer ?)
- Recommended as comonomers to tune properties of high performance polymers

Portfolio	No.s
Publications	25
Patents	10
Review articles	1
Book Chapter	1
PhD Theses	7
Industrial Projects	5

Chapter 9
Step-Growth Polymers from Cashew Nut Shell Liquid (CNSL)-Based Aromatic Difunctional Monomers

CNSL/Cardanol: Market Drivers and Opportunities

- Gels
- Nanoparticles
- Dyes
- Oil additives
- LC polymers
- Bio-oil
- Antimicrobial agents
- Raw materials for drugs
- Thermoplastics
- Anti-oxidants
- UV stabilizers

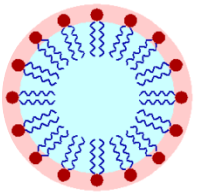


Proof of concept demonstrated

- Addition monomers
  - Acrylates
  - Acrylamides
  - Vinyl ethers
  - Alkyl ethers
- Step growth monomers
- ROP monomers

- Epoxies
  - Foundry
  - Paints and coatings
  - Break liners
  - Adhesives
  - Varnishes and lacquers
- Epoxy diluents
- Phenalkamine curing agents
- PF resins: Laminates
- Surfactants
  - Emulsion/latex
- Polyurethanes
  - Polyols
  - Blocking agents
- Plasticizers
- Rubber additives
  - Flame retardants
  - Processing aids
- Doping agents
- Antistatic agents
- Thermosetting resins
- Modifying agents
- Antitermite agent
- Anti ageing active agent



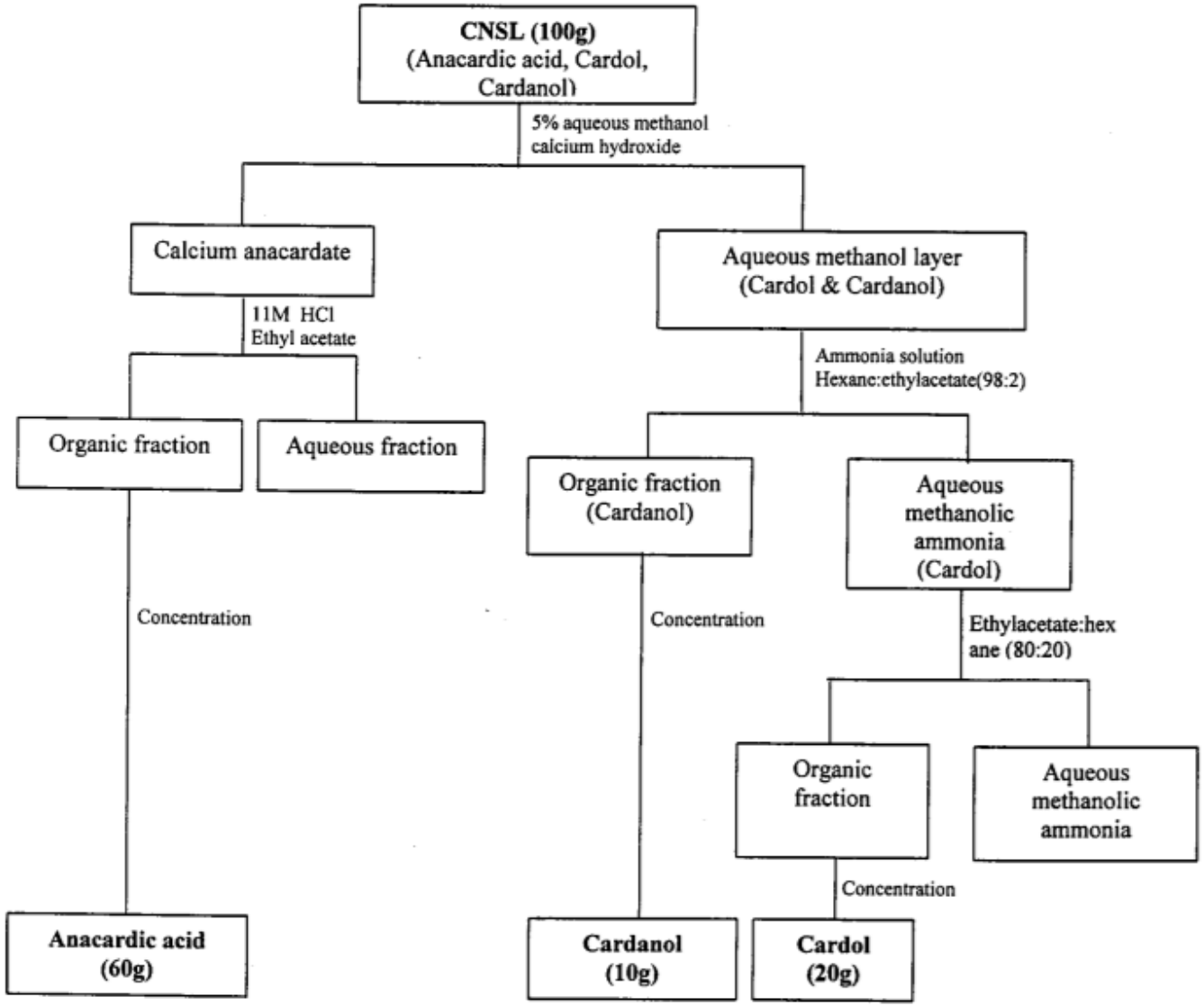



CNSL/Cardanol: Future Prospects for INDIA

- Local availability of Cashew processing industries.
- Established logistics network for cashew nut shell and CNSL.
- Availability of rich and diversified knowledge base in Indian academia.
- Four decades of CNSL handling experience in industry sector.
- Pro-industry government policies.
- Generation of budding entrepreneurs ready to take risk.
- Emerging opportunities for bio-based products in niche applications.
- India has a great opportunity to aggressively pursue CNSL value addition projects.

Thank You

Isolation of CNSL components



- Cold press sample is used for the isolation of **Anacardic acid** as calcium salt
- **Cardanol** is isolated from the Technical CNSL via distillation
- **Cardanol** and **Cardol** isolation from cold press sample is successful in small scale. Scale up investigations under process

CNSL Reports

ACTA SCIENTIFIC AGRICULTURE (ISSN: 2581-365X)

Volume 4 Issue 3 March 2020

Book Review

Case Study: Opportunities and Potential of Cashew Trade Between India and Guinea Bissau 2018

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Published: February 19, 2020

Introduction

Cashew is an important commodity in the international trade spread across the continents and is a major foreign exchange earner to many countries in the world including India. It provides

shews represent 90 percent of the country's exports and the principal source of income in rural areas. Unfortunately, cumbersome administrative arrangements, weak legal systems, and an absence of credit often lead to high transaction costs for cashew buyers

Small-scale cashew nut processing

S H Azam-Ali and E C Judge

ITDG
Schumacher Centre for Technology and Development
Bourton on Dunsmore, Rugby, Warwickshire, UK

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We would also like to thank the small-scale cashew processors in Sri Lanka and the participants of the International Cashew Workshop "Cashing in on Cashew" held in Sri Lanka (November 2000) for sharing vital information on cashew processing.

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E C Judge
Agro-processing Researcher
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Contributions from:
J Gunasekara
Agro-processing Programme Manager
ITDG South Asia
5 Lionel Edirisinghe Mawatha,
Kirulapone, Colombo 5, Sri Lanka

States	Processing Units (Number)	Capacity (000'MT)	Total
Tamil Nadu	453	400	519
Kerala	487	600	387
Andhra Pradesh	184	100	92
Karnataka	276	300	65
Goa	51	50	21
Maharashtra	2260	50	20
Odisha	216	100	15
NE states	27	10	11
West Bengal	46	8	8
Total	4000	1610	1138
Source: CEPCI (2016-17).			

Table 9: Processing Units in India and capacity utilization.

States	Process-ing Units (Units)	Capacity (000'MT)	Utilization (000' MT)		
			Local	Import	Total
Tamil Nadu	453	400	294	225	519
Kerala	487	600	67	320	387
Andhra Pradesh	184	100	92	20	92
Karnataka	276	300	45	0	65
Goa	51	50	21	0	21
Maharashtra	2260	50	20	0	20
Odisha	216	100	11	0	15
NE states	27	10	25	0	11
West Bengal	46	8	8	0	8
Total	4000	1610	574	565	1138

Table 6: Total processing plants in India state wise and total utilization of plant capacity.

Sl. No	Country	Quantity (MT)
1	India	301719
2	USA	143256
3	Germany	35930
4	Netherlands	17236
5	UK	16772
6	Australia	16471
7	Canada	14267
8	UAE	10037
9	Japan	8649
10	France	8562

Table 4: Top Ten cashew consuming countries (2017-18).

Value Proposition of Kernel

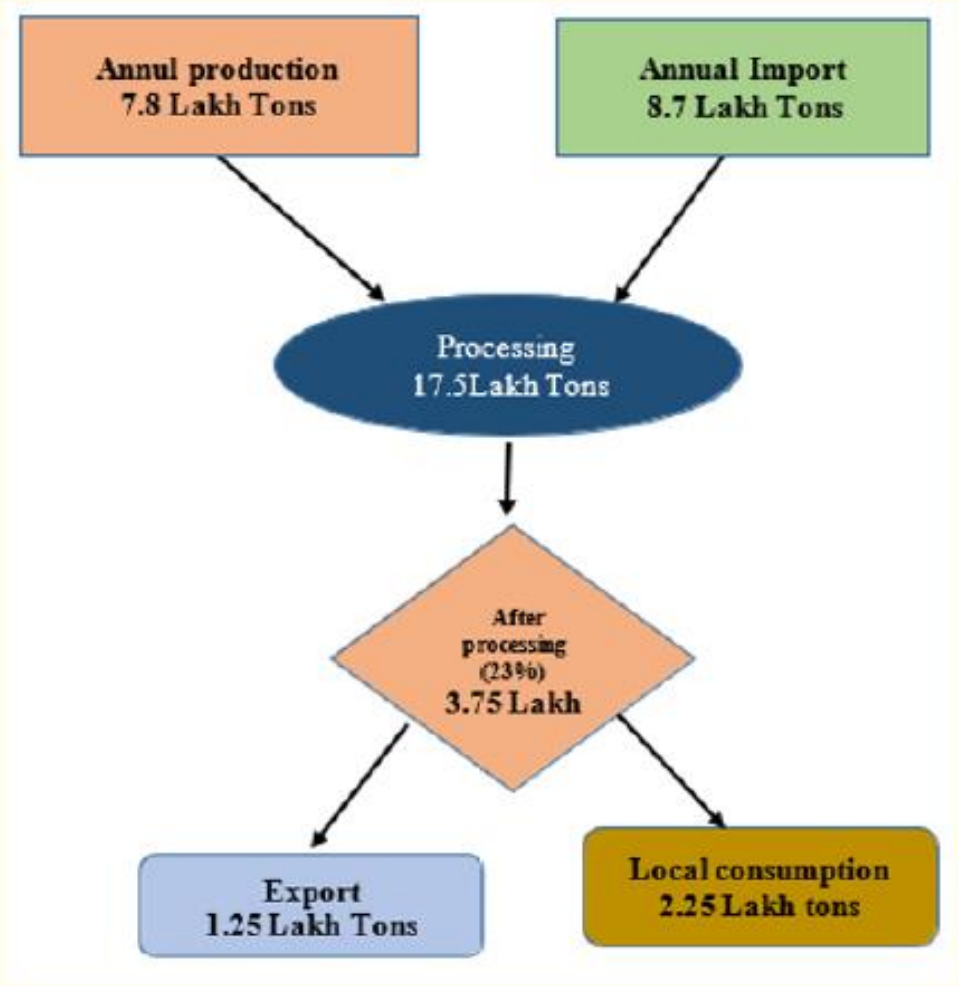

Figure 13: Volume Proposition of cashew in India.