Novel Catalyst for Sustainable Fuel Production

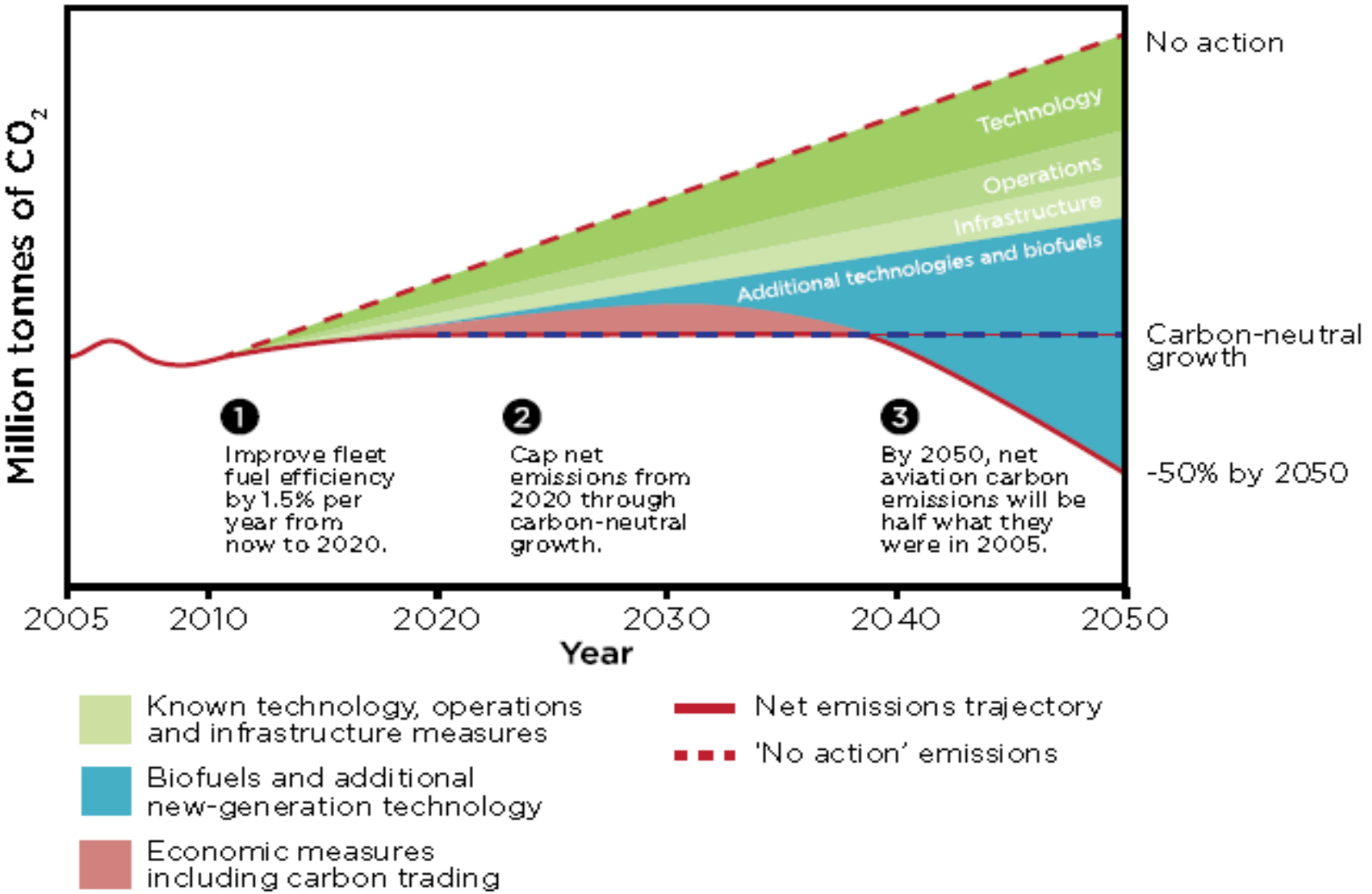
Biofuel Team: Anil K. Sinha, Saleem A. Farooqui, Rakesh Kumar, R. K. Joshi, Rohit Kumar, P. Alam, T. Khan, Dr Anand Narani

Email: farooqui@iip.res.in

Presenter: Mr Saleem Akhtar Farooqui

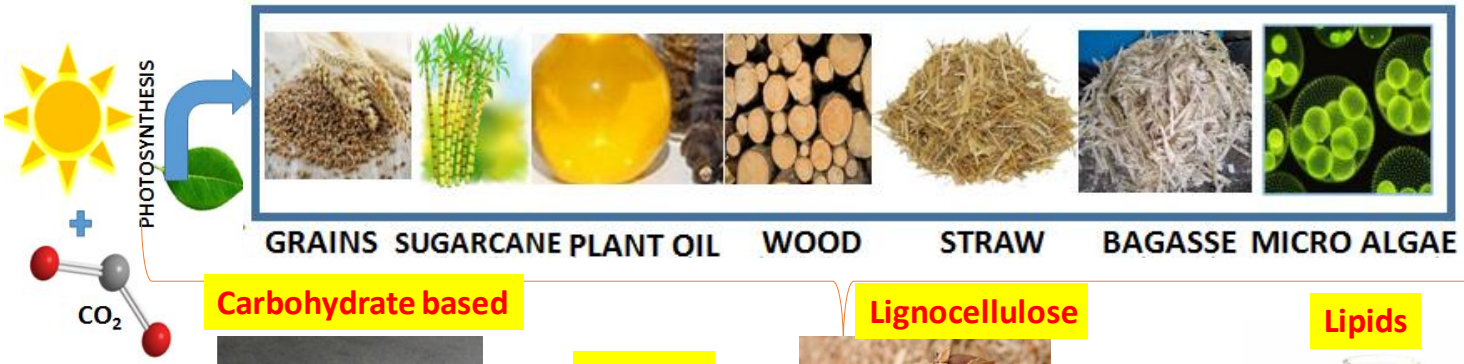
Creating Future Fuels

CO_2 emissions and scenarios



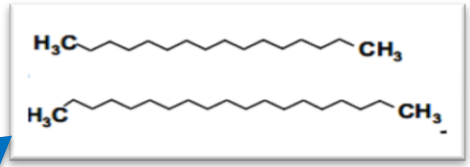
Source: Air Transport Action Group

Biofuels, Technologies-Pathways



CSIR-IIP DILSAAF technology

Two-Reactor Process
Two Catalytic System
(Noble metal - Costly)



Pretreated

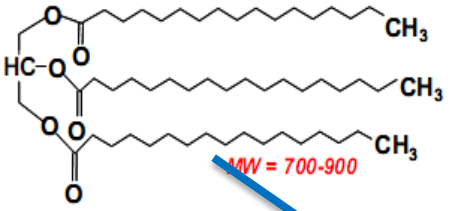
Deoxygenation/Isomerization

Current technologies
(require additional Isomerization/cracking to Jet)

Light Gases
Light HC, H_2 and CO_2

Diesel Range
(C15+)

H_2O



$+H_2$

Na, P, K, Ca, Fe

Pretreater

Deoxygenation/Selective
Cracking/Isomerization

Light Gases
Light HC, H_2 and CO_2

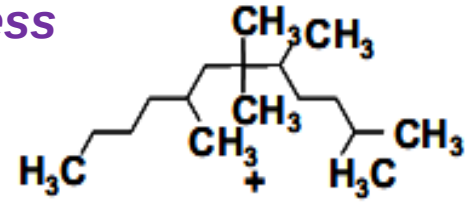
Naphtha (C5-C9)

Bio-Jet Fuel (C9-C15)

Diesel Range (C15+)

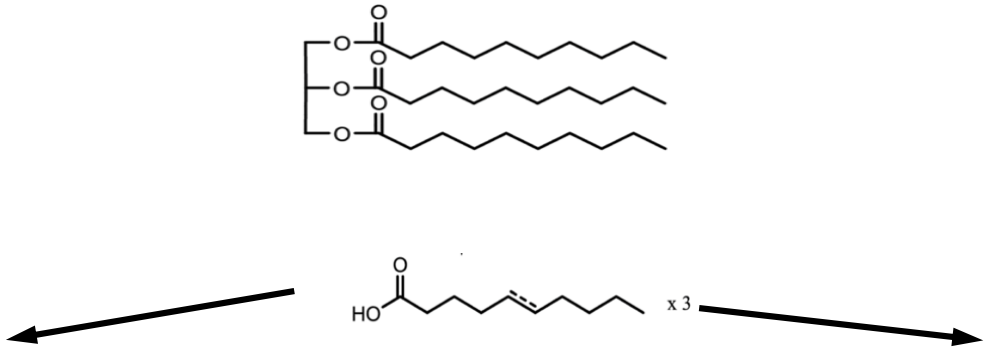
H_2O

Single-Reactor Process
Single Catalyst



CSIR-IIP Technology

Conversion Chemistry-DILSAAF process



Increased flowability

https://doi.org/10.1016/j.cattod.2017.12.021
10.1007/s10563-012-9148-x

CSIR-IIP Proprietary Catalyst

Creating Future Fuels

Single Step Novel Process and Catalyst (Non noble metal)

(1) Hydro-deoxygenation

(2) Hydro-cracking

(3) Hydro-isomerisation

(4) Aromatization

(5) Hydro-cyclization

(6) Hydrogenation

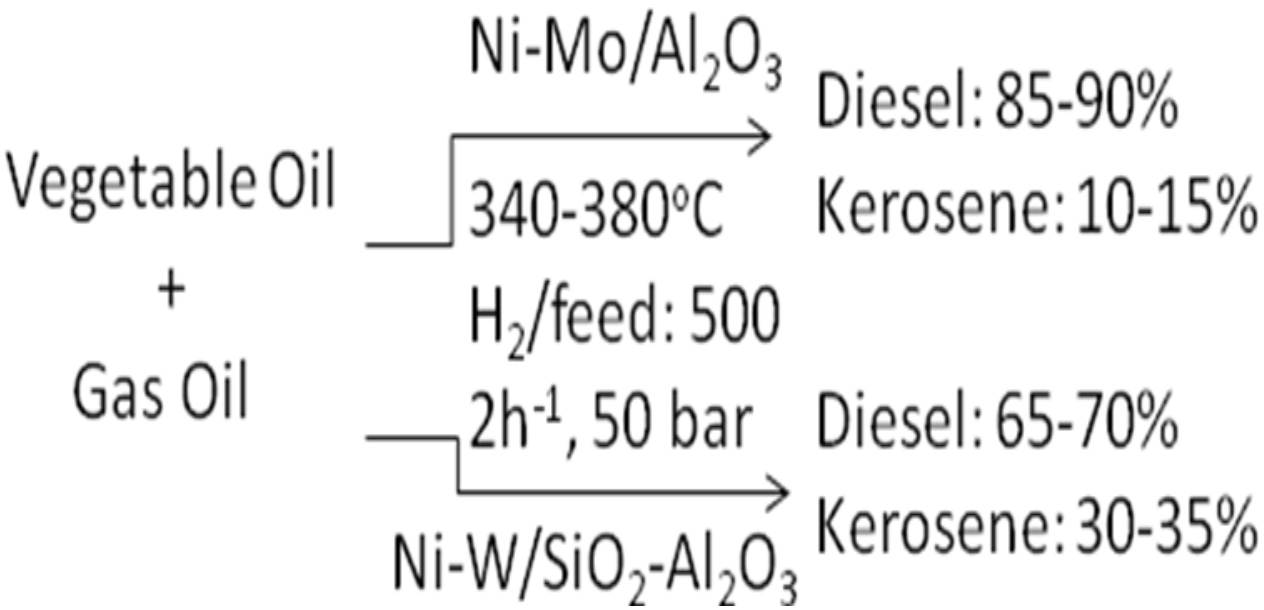
Catalyst features

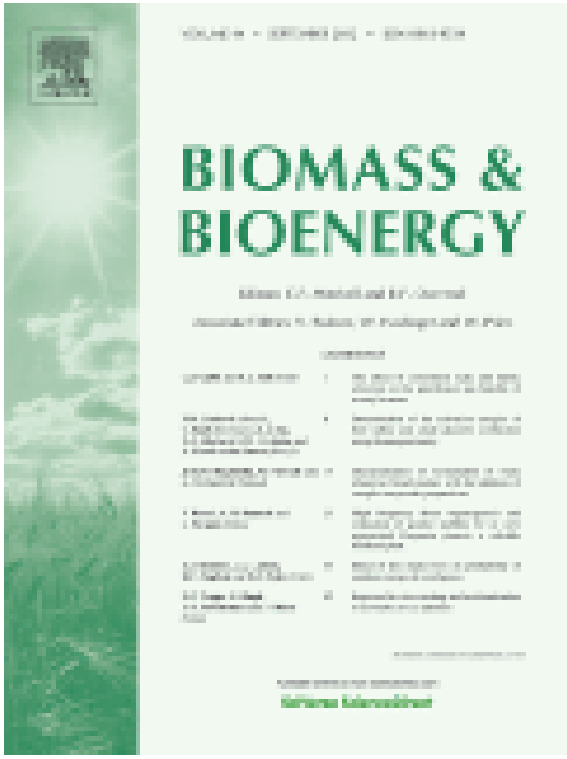
- **Porous silica-alumina** based support with **optimized Brönsted – acidity**
- **Controlled Si/Al ratio** for desirable **cracking and isomerization ability** to maximize the kerosene range
- Sulfided base-metal (**non-noble) catalyst** with **maximum dispersion** and loading on the silica-alumina support (**lower in cost as** compared to completive technologies)

Co-processing of vegetable oil

Creating Future Fuels

Transportation Fuels from Co-Processing of Waste Vegetable Oil and Gas Oil Mixtures using Mesoporous Catalyst Supports





Biomass and Bioenergy, Volume 56, September 2013, Pages 43-52; https://doi.org/10.1016/j.biombioe.2013.04.029

Hydroprocessing of jatropha oil and its mixtures with gas oil†

Rohit Kumar, Bharat S. Rana, Rashmi Tiwari, Deepak Verma, Rakesh Kumar, Rakesh K. Joshi, Madhukar O. Garg and Anil K. Sinha*

Received 11th June 2010, Accepted 18th October 2010
DOI: 10.1039/c0gc00204f

340-380°C, H_2/feed: 1500, 1-2h^{-1}, 50

Jatropha Oil + Gas Oil → $Ni\text{-}Mo/Al_2O_3$ → Diesel: 88-92%

Diesel : 98%

Jatropha Oil → $Co\text{-}Mo/Al_2O_3$ → Diesel : 49%, Kerosene: 36%

$Ni\text{-}W/SiO_2\text{-}Al_2O_3$ → Diesel: 81%

Sulfided Ni-Mo - hierarchical mesoporous H-ZSM-5 high yield of jet fuel from jatropha and algal oil

Creating Future Fuels

NiMo-H-ZSM-5(Meso)
410^{0}C, 50bar, 1hr^{-1}

NiMo-H-ZSM-5(Meso)
400^{0}C, 80bar, 1.1hr^{-1}

NiMo-H-ZSM-5(Meso)
410^{0}C, 50bar, 1hr^{-1}

Jet range(C9-C15) Yield(%) and i/n ratio

78.5% and 2.5

38.3% and 13.5

54.0% and 2.6

Deepak Verma, Rohit Kumar, Bharat S. Rana and Anil K. Sinha, ***Energy Environ. Sci.,*** *2011, 4, 1667*

Catalyst Screening

Hydrocoversion of Jatropha and Algal Oil over Sulfided Ni-Mo - Hierarchical Mesoporous H-ZSM-5

CATALYST	FEED	T(^{0}C)	P(bar)	Yield% (C_9-C_{15})	CONV. (%)	#i/n RATIO
1) Ni-W/SiO_2-Al_2O_3 (micro-mesoporous)	Jatropha oil	420	80	33.2	99	1.1
2) Ni-W/H-ZSM-5 (micro-mesoporous) HSASC**	Jatropha oil	400	60	39.6	99	5.2
3) Ni-Mo/H-ZSM-5 (micro-mesoporous) -LSAC	Jatropha oil	400	80	38.3	99	13.5
		380	80	42.7	96	4.9
4) Ni-Mo/H-ZSM-5 (micro-mesoporous) HSASC**	Jatropha oil	410	50	54.3	96	2.6
	Algae oil	410	50	78.5	98	2.5

#ratio of isomers (i) and normal (n) alkanes, *LSAC=Low Surface Area Crystalline, **HSASC=High Surface Area Semi Crystalline, lhsv = 1h^{-1}

Optimization of catalyst hydrogenation functionality for Hydroprocessing of Non-edible oils into Biofuels

Catalyst loading and reaction operating conditions

Catalyst	NiMo-7	NiMo-11	NiMo-15
Catalyst Mass, g	3	2	3
Catalyst Volume, ml	5.5	3.5	5.5
Bed length, cm	7.0	4.5	7.0
Catalyst shape	Trilobes Extrudates (3-5 mm length)		
Processing conditions			
Reaction Temperature, ^{o}C	340 – 420		
Reaction pressure, Bar	80 – 90		
LHSV, hr^{-1}	0.5 – 2		
H_2/FEED, Nl/L	1500-2500		
H_2/FEED, molar ratio	63-105		

Three different NiMo-7, NiMo-11, and NiMo-15 catalysts were evaluated under different operating reaction conditions

Physicochemical properties of catalysts

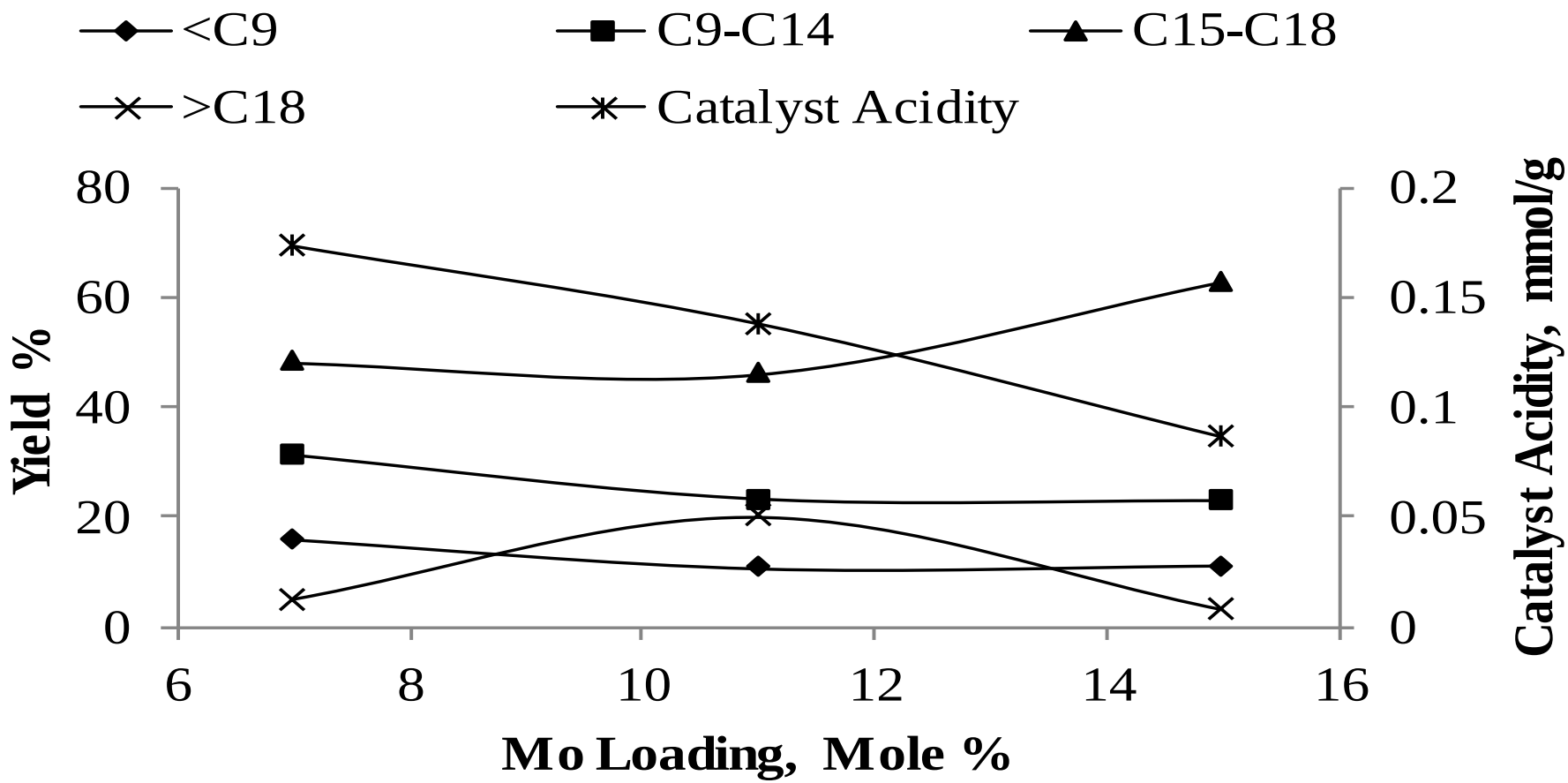
Catalyst	Surface area (m^2/g)	Total Pore Volume (cm^3/g)	Mean pore diameter (nm)	Total surface acidity[a] NH_3 (mmol/g)	Brønsted acid sites[b] (mmol/g)	Lewis acid sites[b] (mmol/g)	L/B
NiMo-7	219	0.55	10.4	0.173	0.08	0.093	1.16
NiMo-11	190	0.53	9.9	0.138	0.08	0.058	0.72
NiMo-15	188	0.47	9.5	0.087	0.055	0.032	0.58

[a] NH_3 temperature-programmed desorption (TPD), [b]acidity measured by pyridine FT-IR

- ✓ The ratio of Lewis to Brönsted acid (L/B) sites at different loading decreased with an increase in Mo loading, i.e., NiMo-7(L/B:1.16) > NiMo-11(L/B:0.72) > NiMo-15(L/B:0.58).

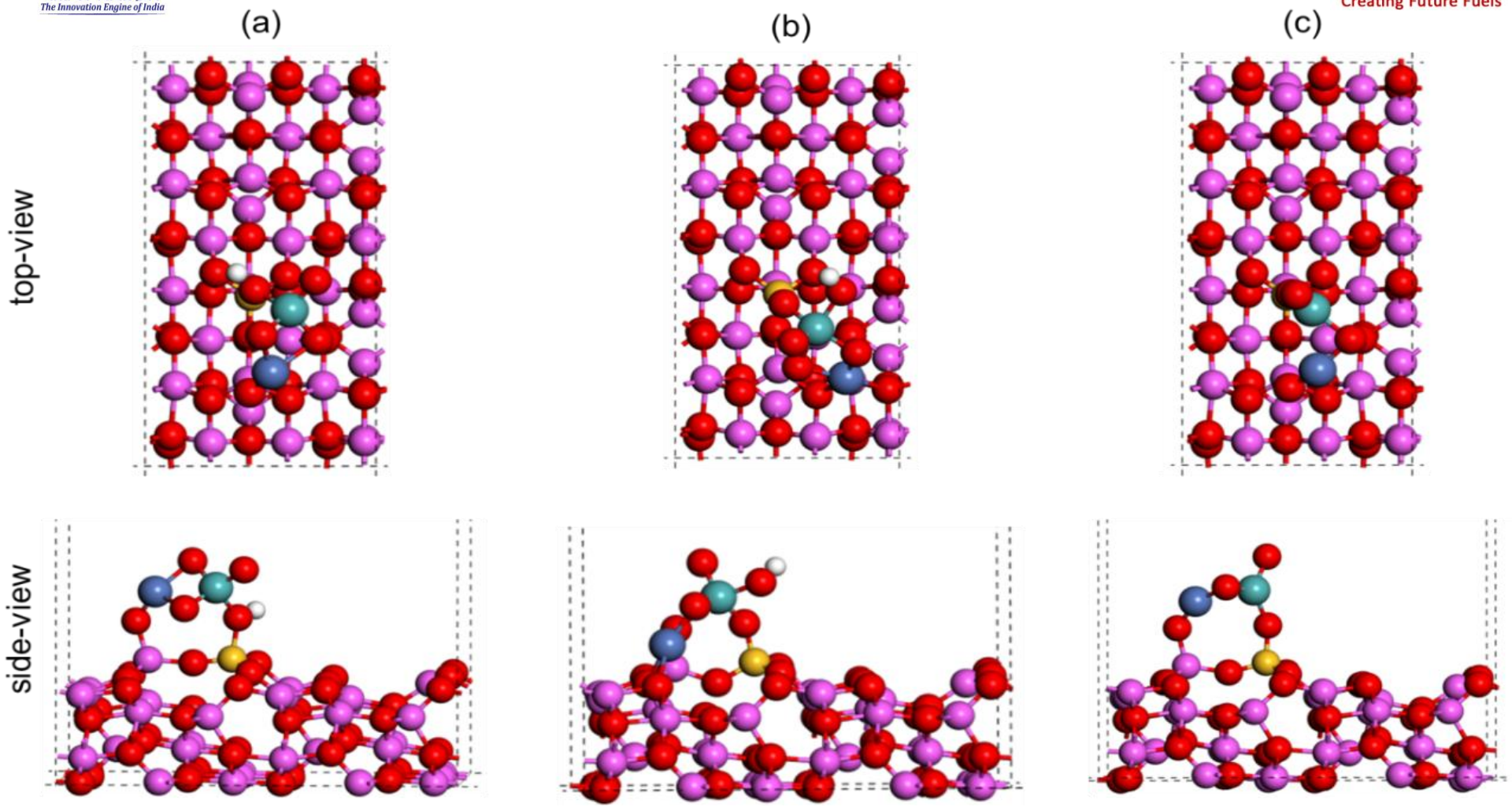
- ✓ The increased Lewis acidity for NiMo-7 compared to NiMo-11 and NiMo-15 was anticipated due to the increased availability of adsorption/desorption sites on the silica-alumina surface.

Product mean yield as a function of Mo loading



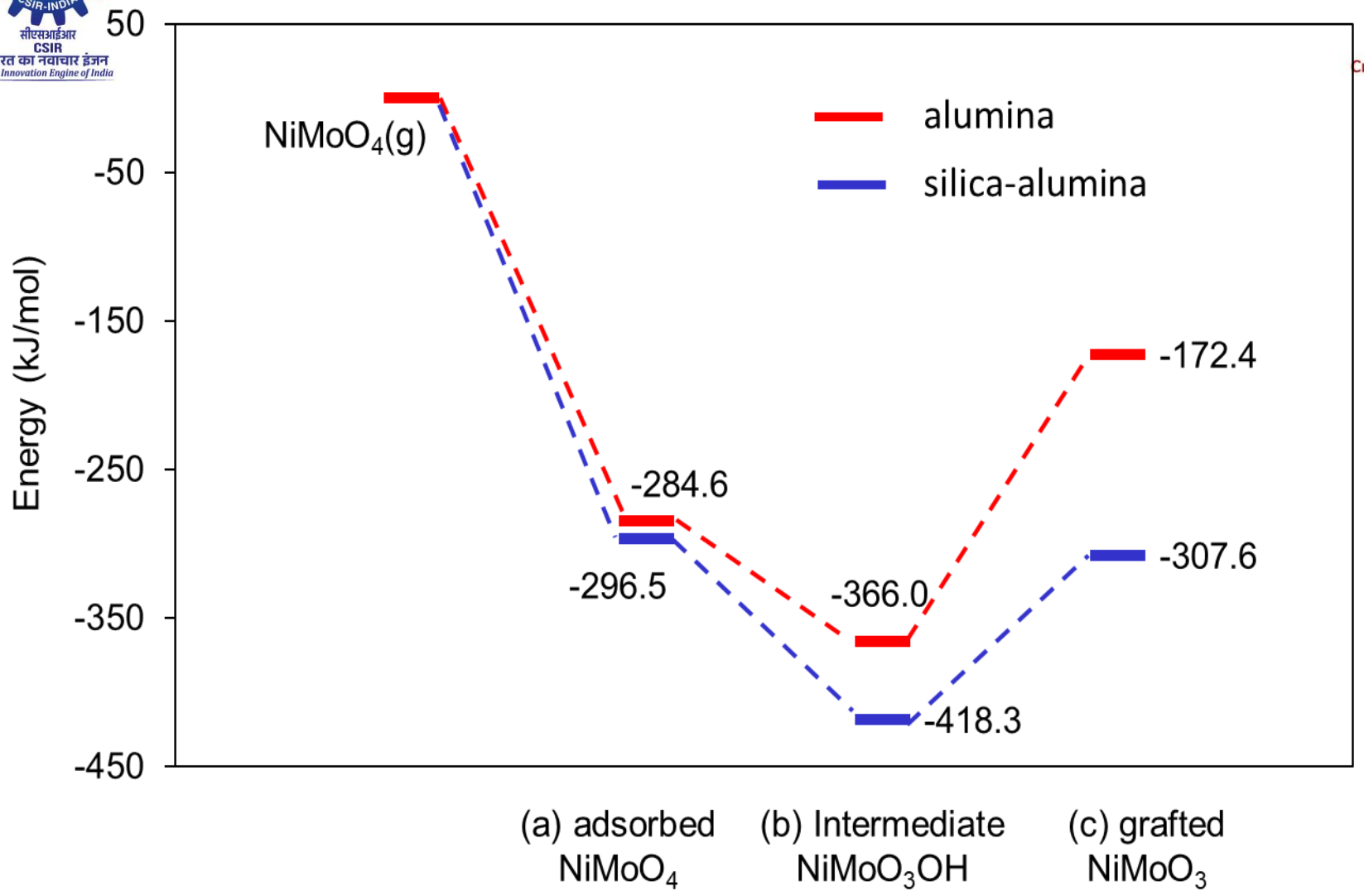
5% Ni/Si-doped Alumina, 420 °C, 80 bar, 1 hr^{-1}, at A:1500 Nl/L

Adsorption and grafting of the NiMoO4 cluster at the silica-alumina surface



(a) adsorption of $NiMoO_4$, (b) transfer of Brønsted H to $NiMoO_4$, (c) grafting of $NiMoO_3$ after removal of H_2O. Color code: Al (pink), O (red), H (white), Ni (blue), Mo (bluish-green).

Reaction energy diagram

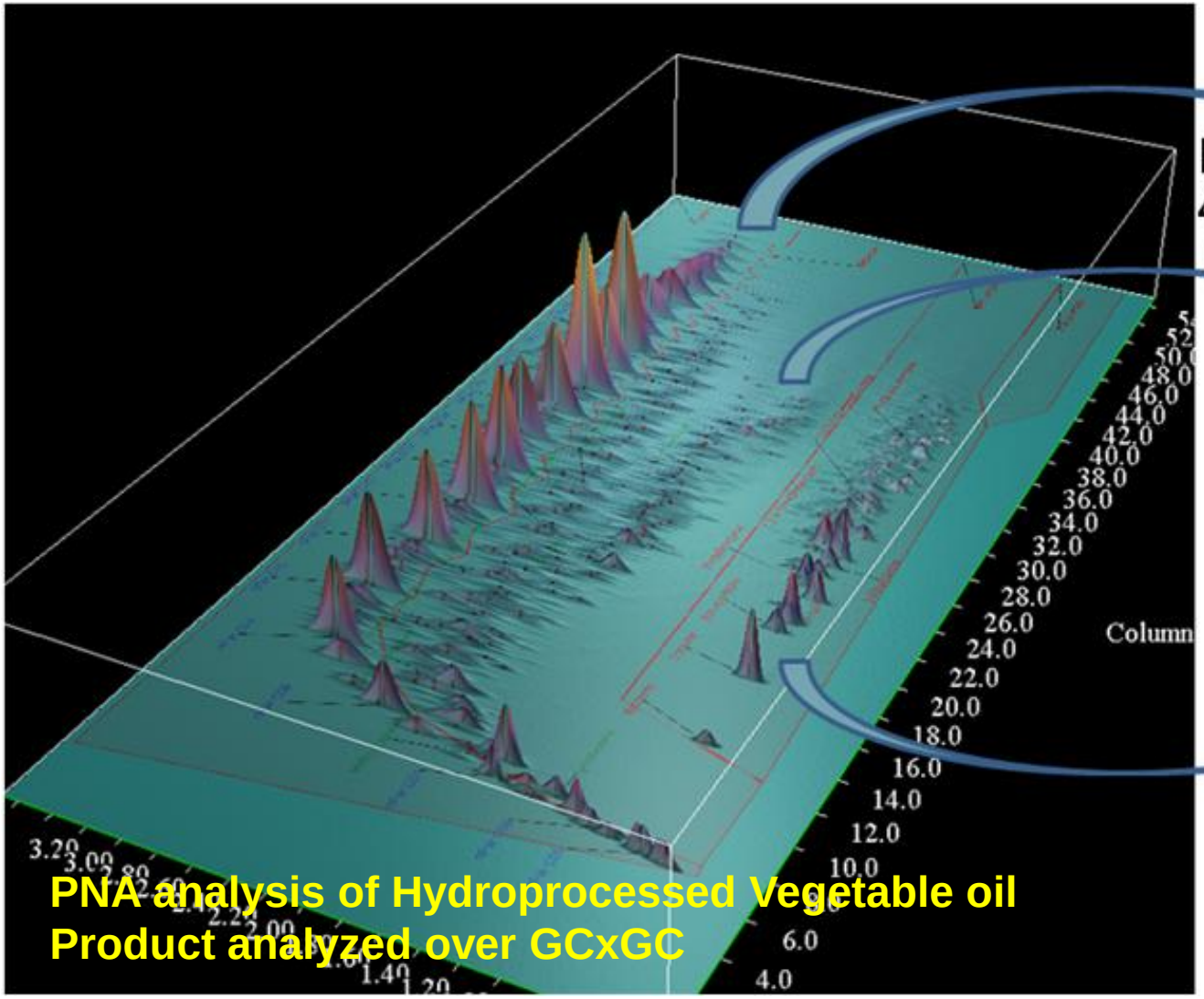


Reaction energy diagram for the adsorption and grafting of the $NiMoO_4$ nanocluster at the alumina and silica-alumina surface Brønsted acid site.

Hydroconversion of Jatropha oil to hydrocarbon over Pt encapsulated $NiMo/SiO_2$-Al_2O_3

Aromatics in Hydroprocessed Vegetable oil

Creating Future Fuels

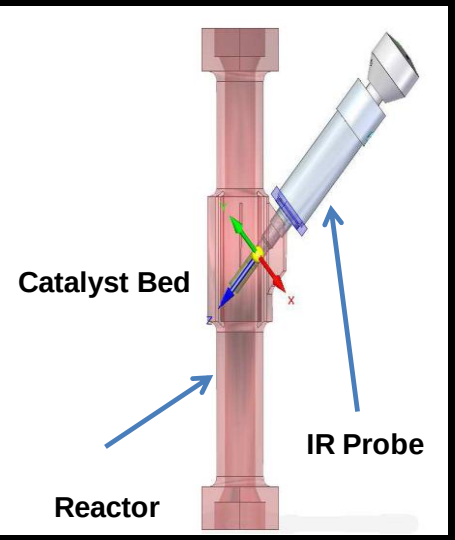


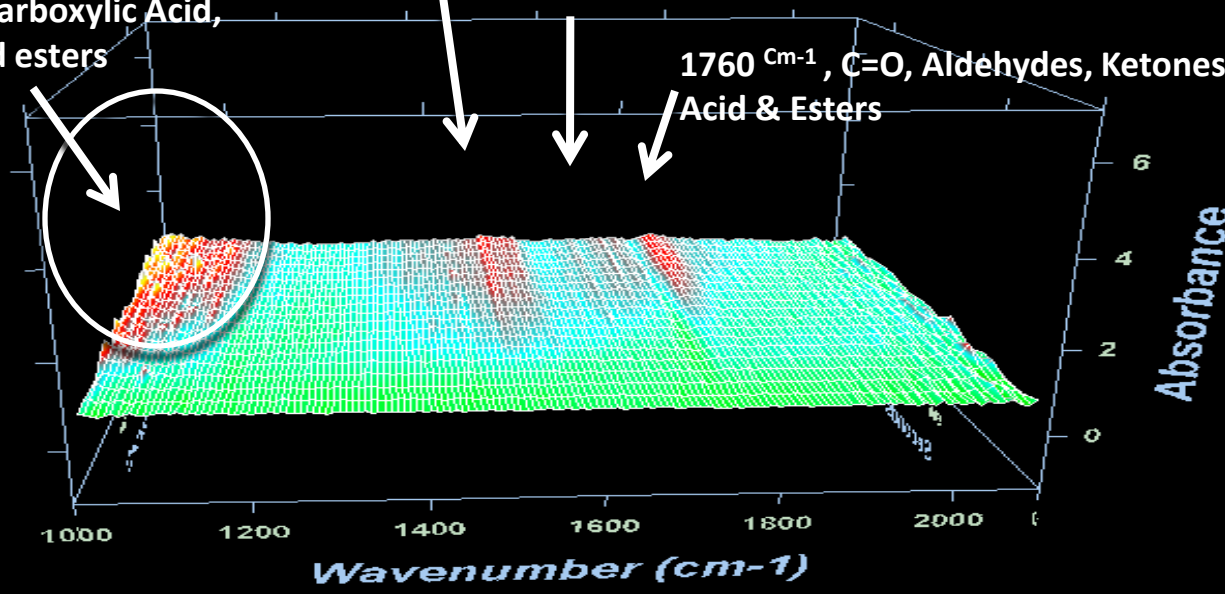
1500 Cm-1 , C=C, Aromatic Ring

1000-1200 Cm-1 , C–O , Alcohol, Carboxylic Acid, ethers and esters

1640-1680 Cm-1 , C=C, Alkenes

1760 Cm-1 , C=O, Aldehydes, Ketones, Carboxylic Acid & Esters



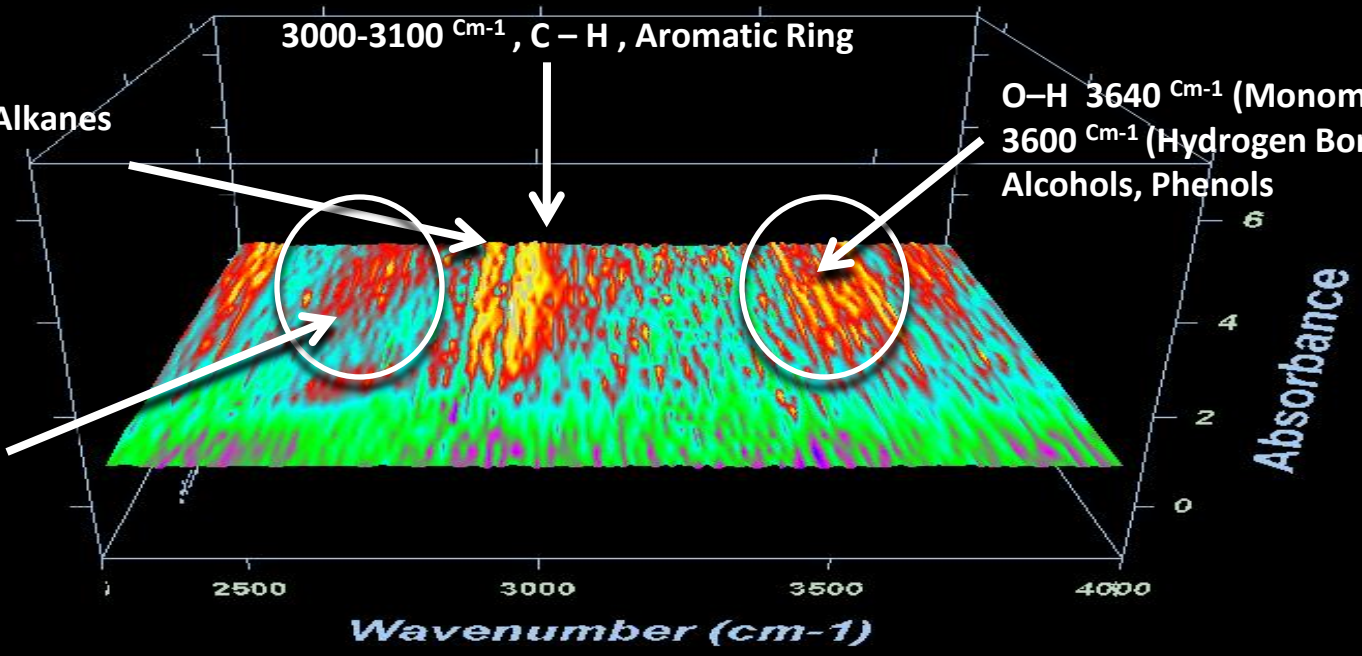


3000-3100 Cm-1 , C – H , Aromatic Ring

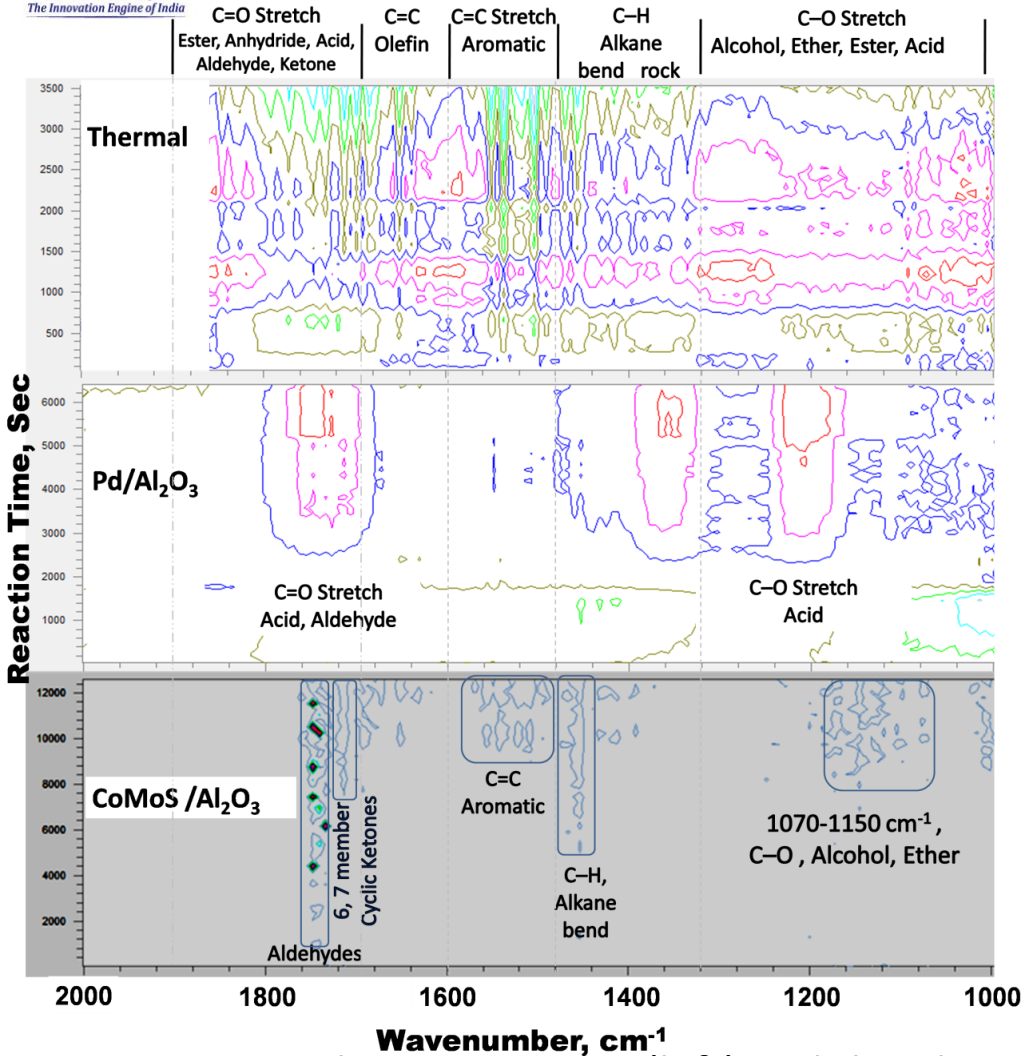
2850-2960 Cm-1 , C – H , Alkanes

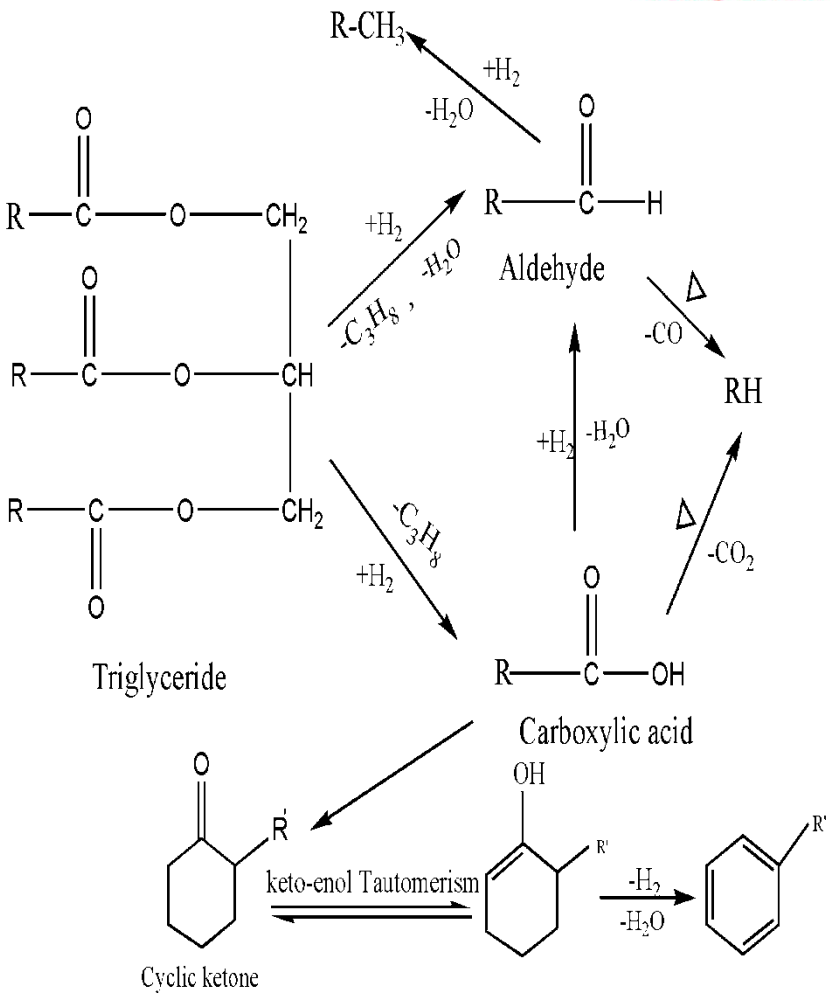
O–H 3640 Cm-1 (Monomeric), 3600 Cm-1 (Hydrogen Bonded) , Alcohols, Phenols

2500-3000 Cm-1 , O–H , Carboxylic Acid



Aromatics formation Mechanism

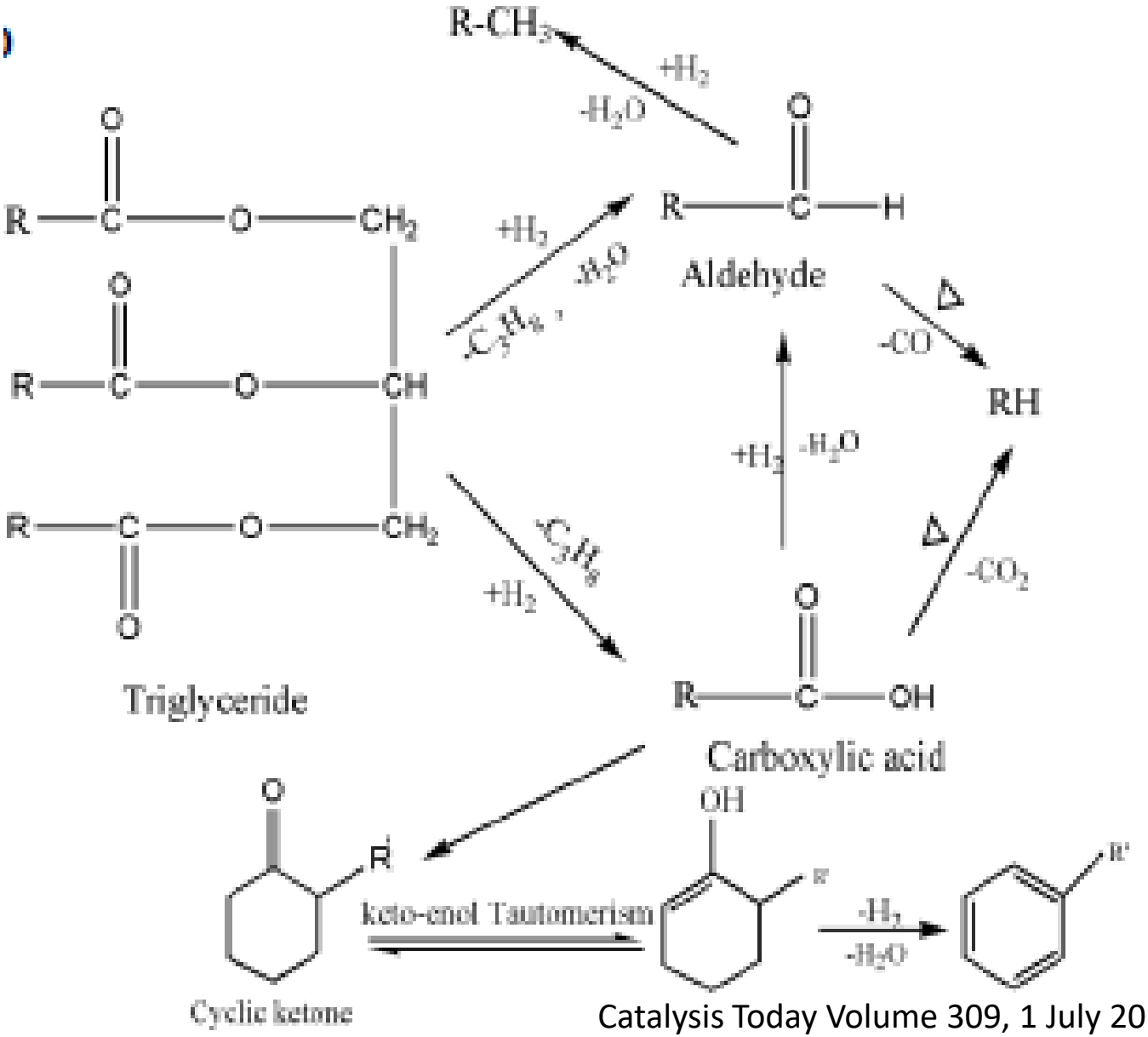




FT-IR spectra with reaction time (left) and the plausible reaction mechanism (right) for the hydroprocessing and hydrogenation of triglycerides

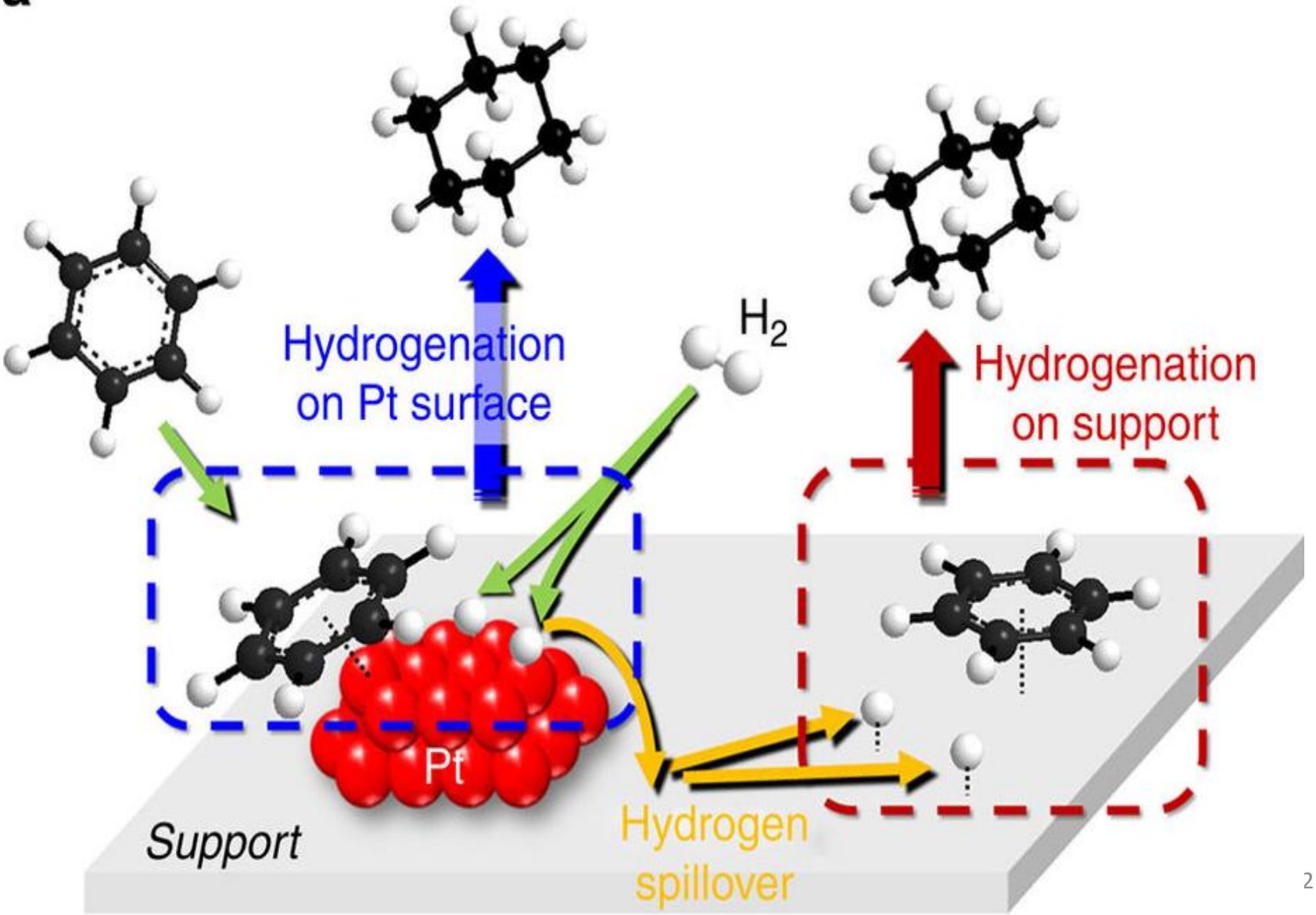
Formation of aromatics via cyclic ketones from acid intermediates is proposed

Proposed Mechanism for triglyceride conversion over $CoMo/Al_2O_3$

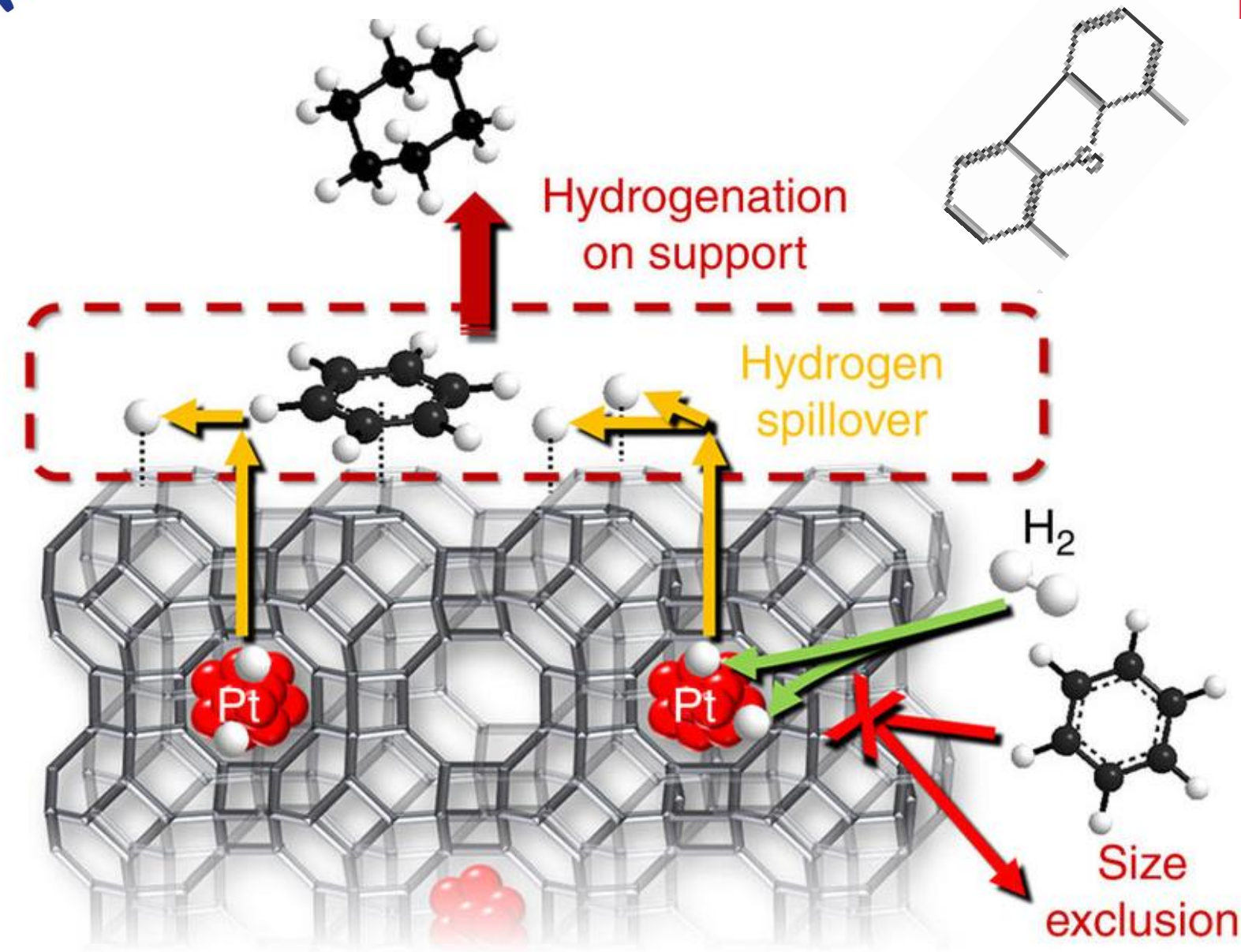


Catalysis Today Volume 309, 1 July 2018, Pages 11-17; https://doi.org/10.1016/j.cattod.2017.12.021

H_2 Spillover mechanism



Reaction Mechanism



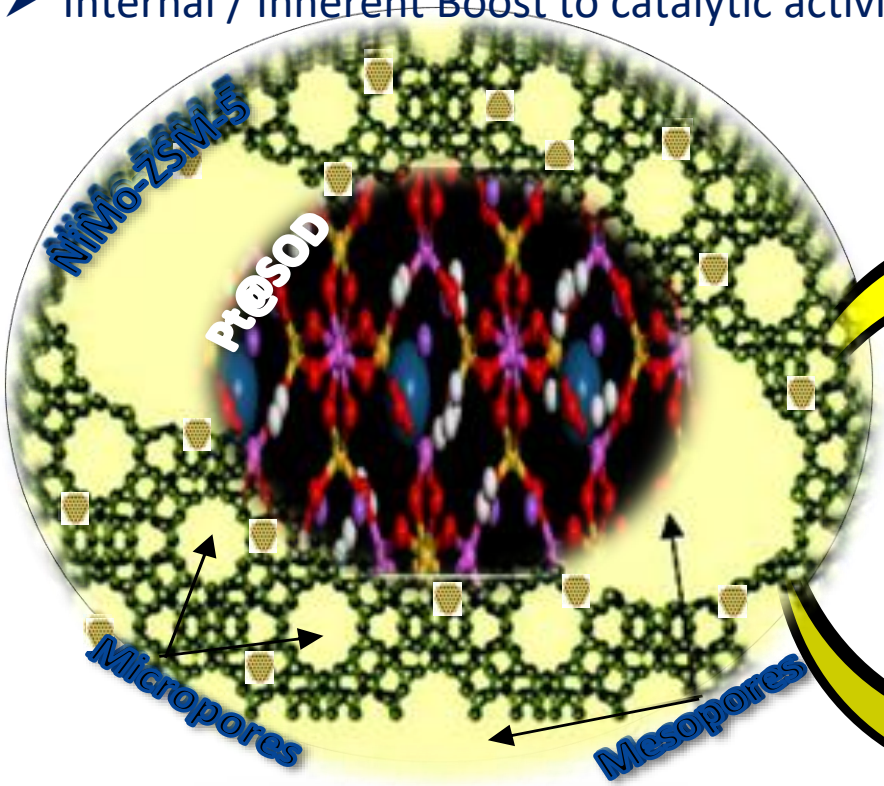
Nature Communications 5, Article number: 3370 (2014)doi:10.1038/ncomms4370

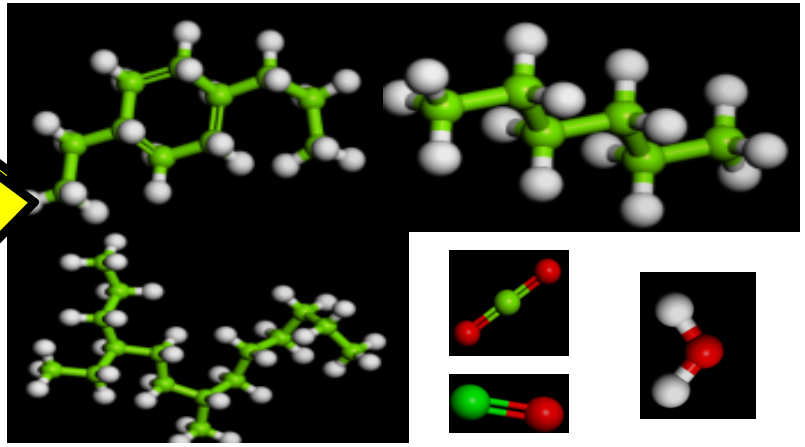
Encapsulated sub-nano-Pt in Zeolite cages

Creating Future Fuels

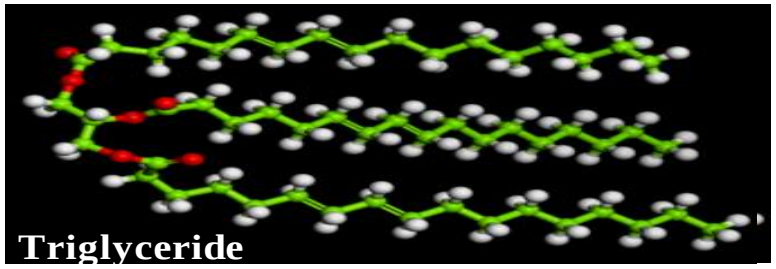
- Active hydrogen to be accessible to reactants
- Active Sites Protected against poisons.
- Internal / Inherent Boost to catalytic activity

Sodalite –Zeolite (access through 2.8 Å window)- 6 mem ring
Cage diameter of 6–8 Å





SOD cage Prevents from Sintering and Permanent Poison >2.8 Å
Hydrogen Spillover – Pt to active metal

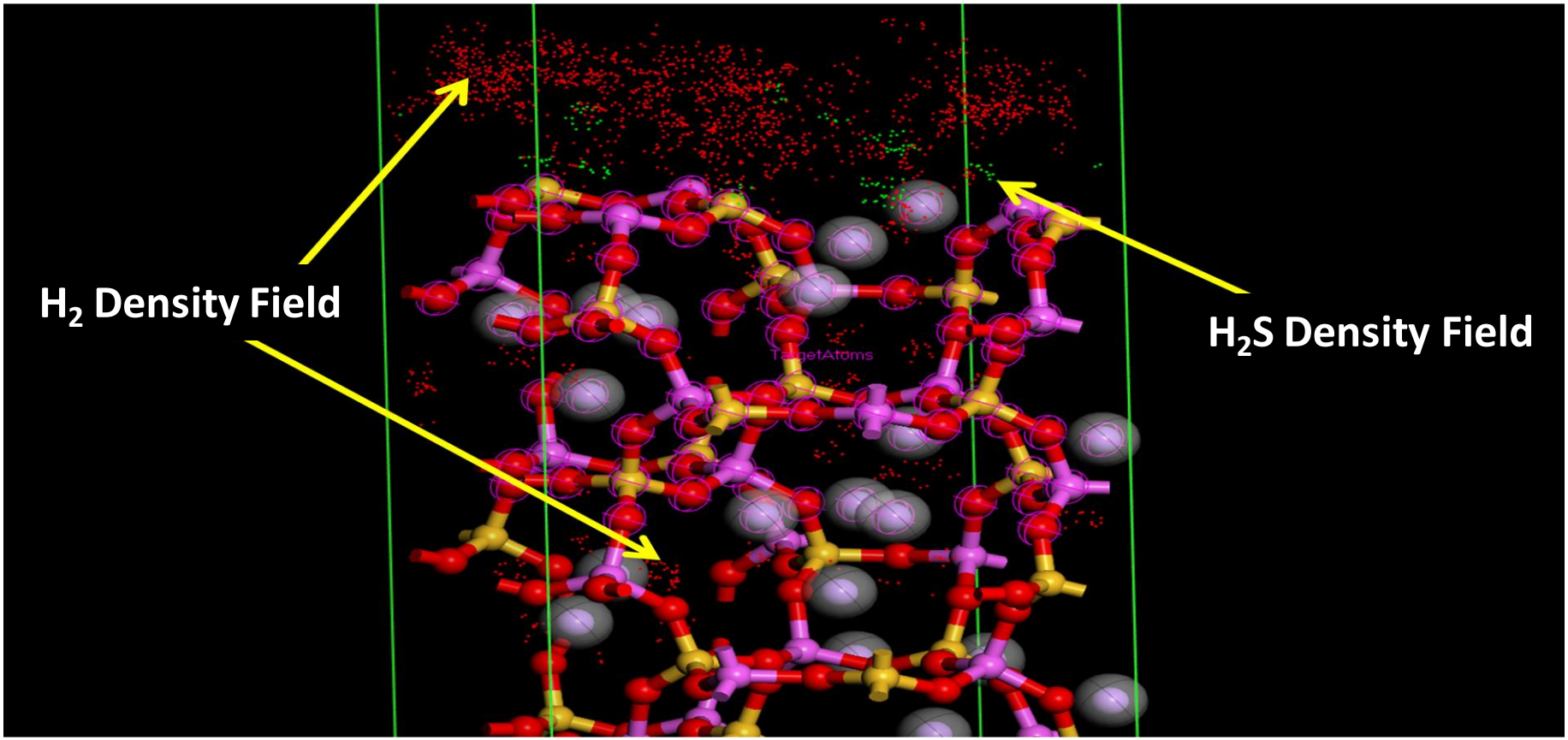


NiMoS
Pt, < 0.8 nm
SOD cage, 0.8 nm
H-ZSM-5

C
O
H

Patent: 4093DEl2015; Catal. Sci. Technol., 2016, 6, 1850-1862

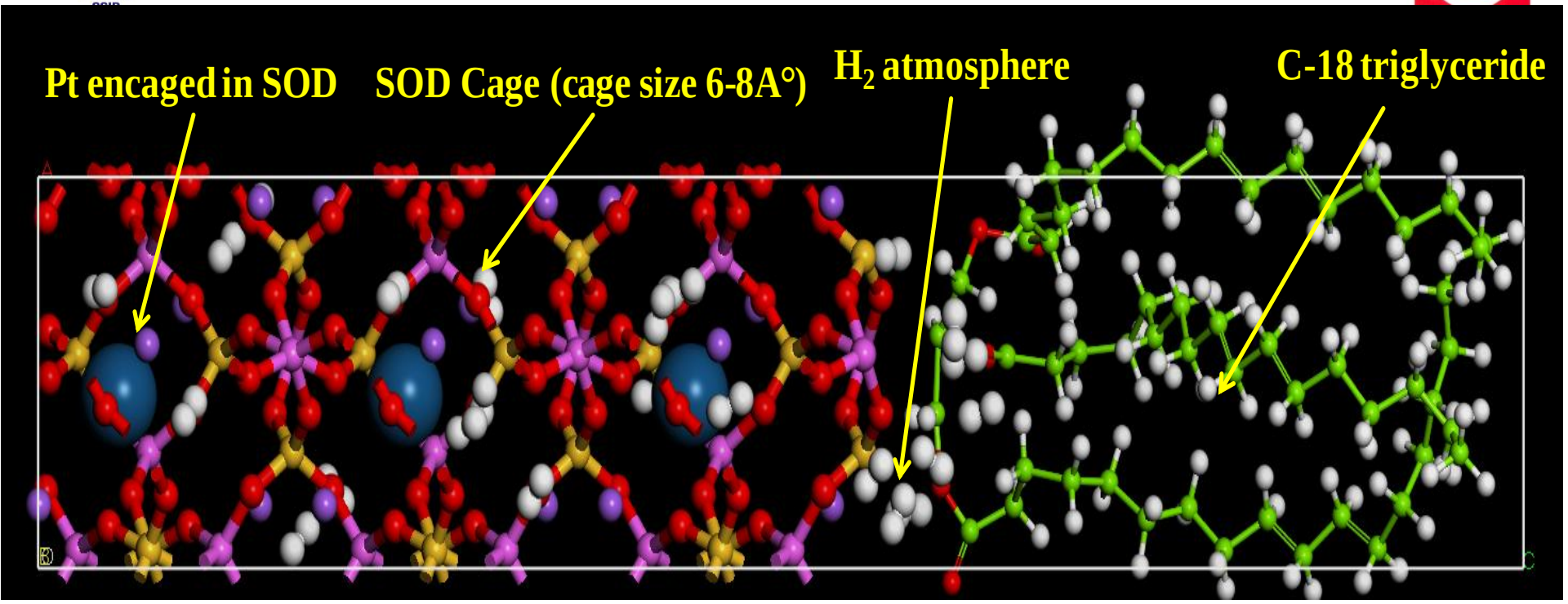
Adsorption Sites of H_2 and H_2S in Sodalite Structure



H_2S density field (green) is completely outside the SOD cage while the H_2 density field (red) is spread all over the SOD cage both inside and outside.

IPO: 4093DEl2015;***Catal. Sci. Technol.***, 2016, **DOI:** 10.1039/C5CY01243K

Triglyceride stabilized on sodalite (SOD) structure

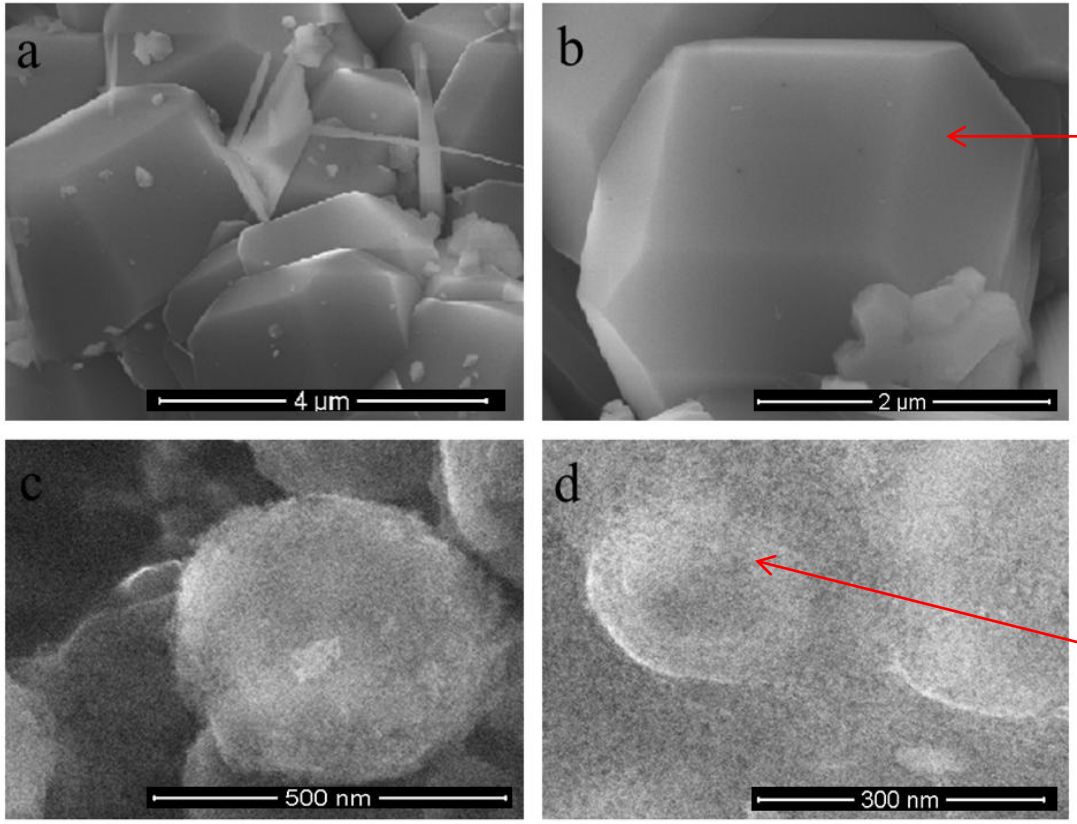


Model element	Interaction Energy, kcal/mol
(TG-SOD-H_2)	-451.6
(TG-Pt@SOD-H_2)	-853.7 (lower)

Indicating *stronger affinity of the feed molecules to the catalyst surface* in presence of Pt which is expected to increase the overall catalytic activity

IPO: 4093DEl2015;***Catal. Sci. Technol.***, 2016, **DOI:** 10.1039/C5CY01243K

FESEM Images of The Catalyst



Clean surface. i.e., all the Pt Clusters are inside the cages

No Pt Clusters Observed on Surface – EDX Elemental Mapping

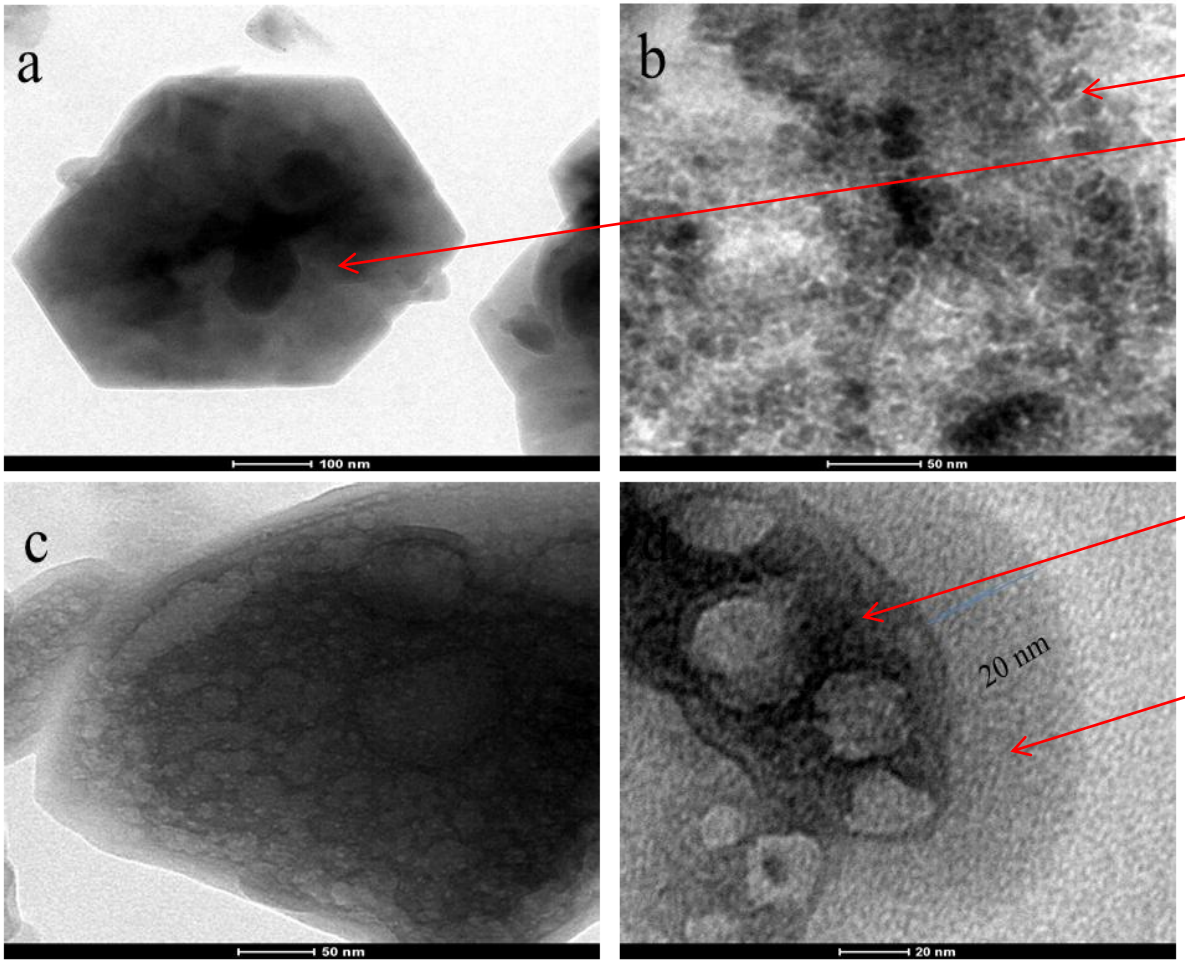
SOD inside ZSM-5

FESEM images of (a) bulk Pt@SOD crystals (b) Exposed Pt@SOD single crystal (c) Pt@SOD@ZSM-5 (d) Enlarged portion of Pt@SOD@ZSM-5

IPO: 4093DEl2015;***Catal. Sci. Technol.***, 2016, **DOI:** 10.1039/C5CY01243K

HRTEM Images Of Pt@SOD@ZSM-5

ICP-AES – Also Confirmed Pt



Pt clusters inside the SOD

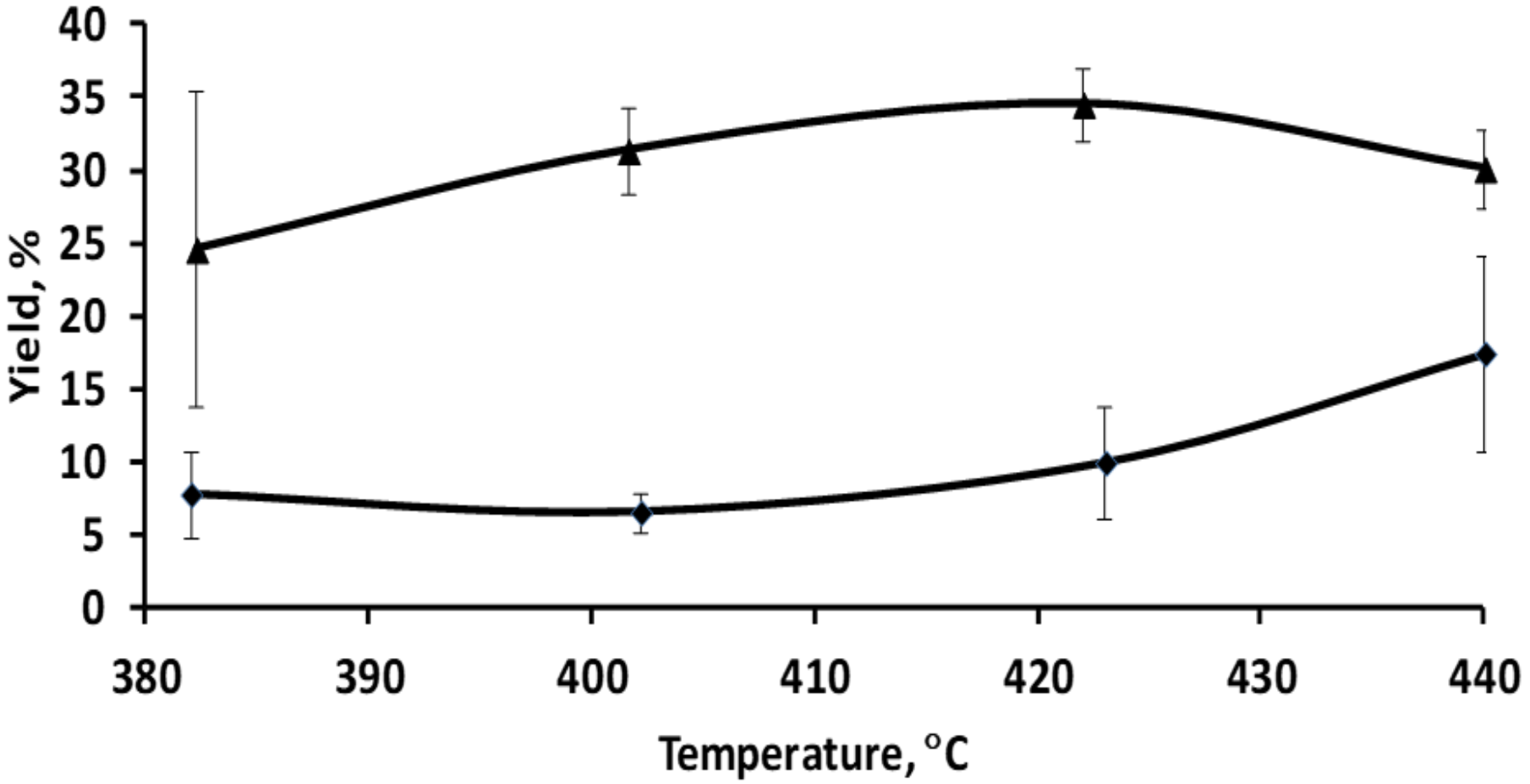
Pt clusters inside the SOD

20 nm zeolitic coating

HRTEM images of (a, b) Pt@SOD (c, d) Pt@SOD@ZSM-5

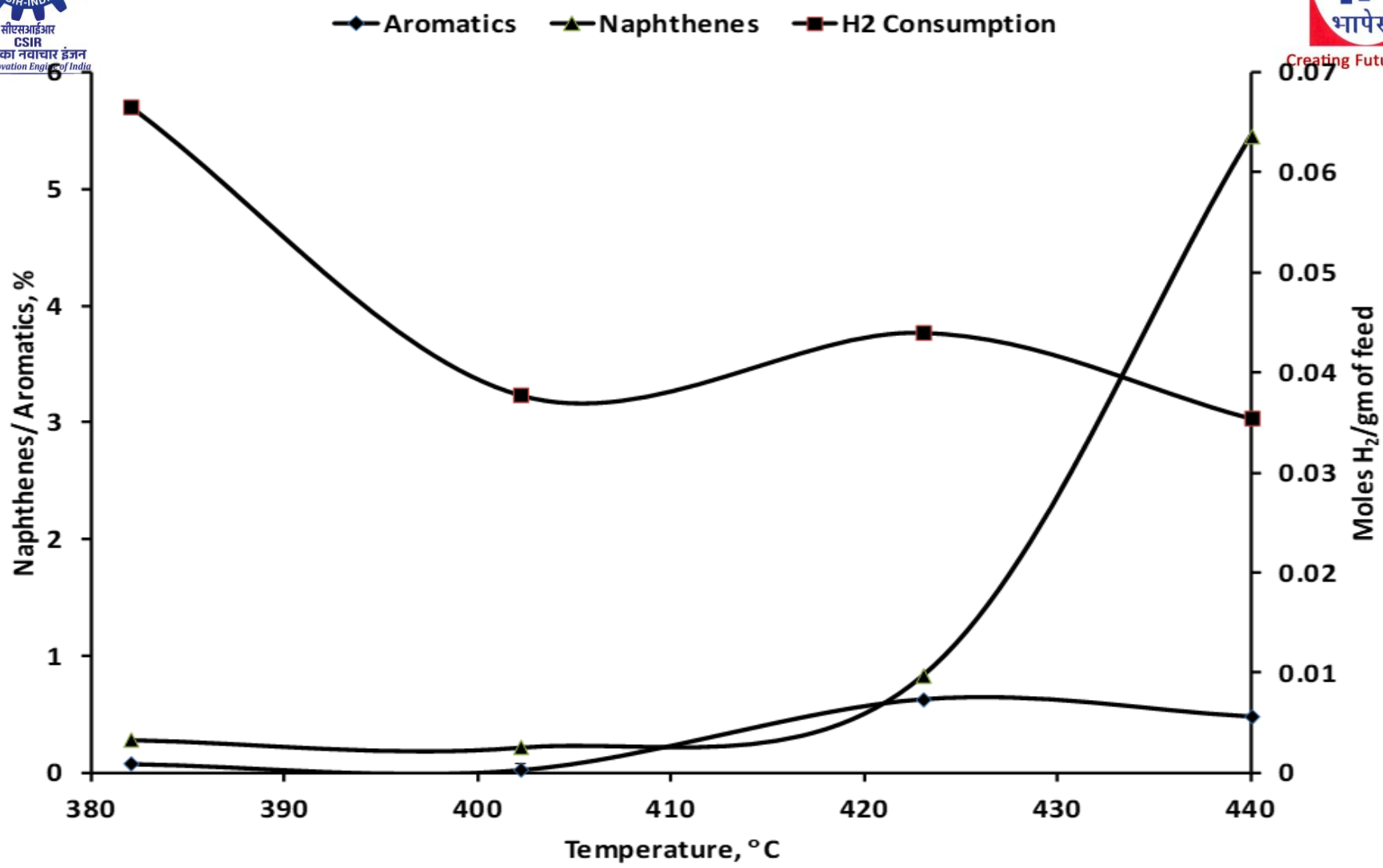
IPO: 4093DEl2015;***Catal. Sci. Technol.***, 2016, **DOI:** 10.1039/C5CY01243K

Mid-range hydrocarbon yield distribution (C9-C15) with temperature Pt@SOD-NiMo-SiO_2-Al_2O_3



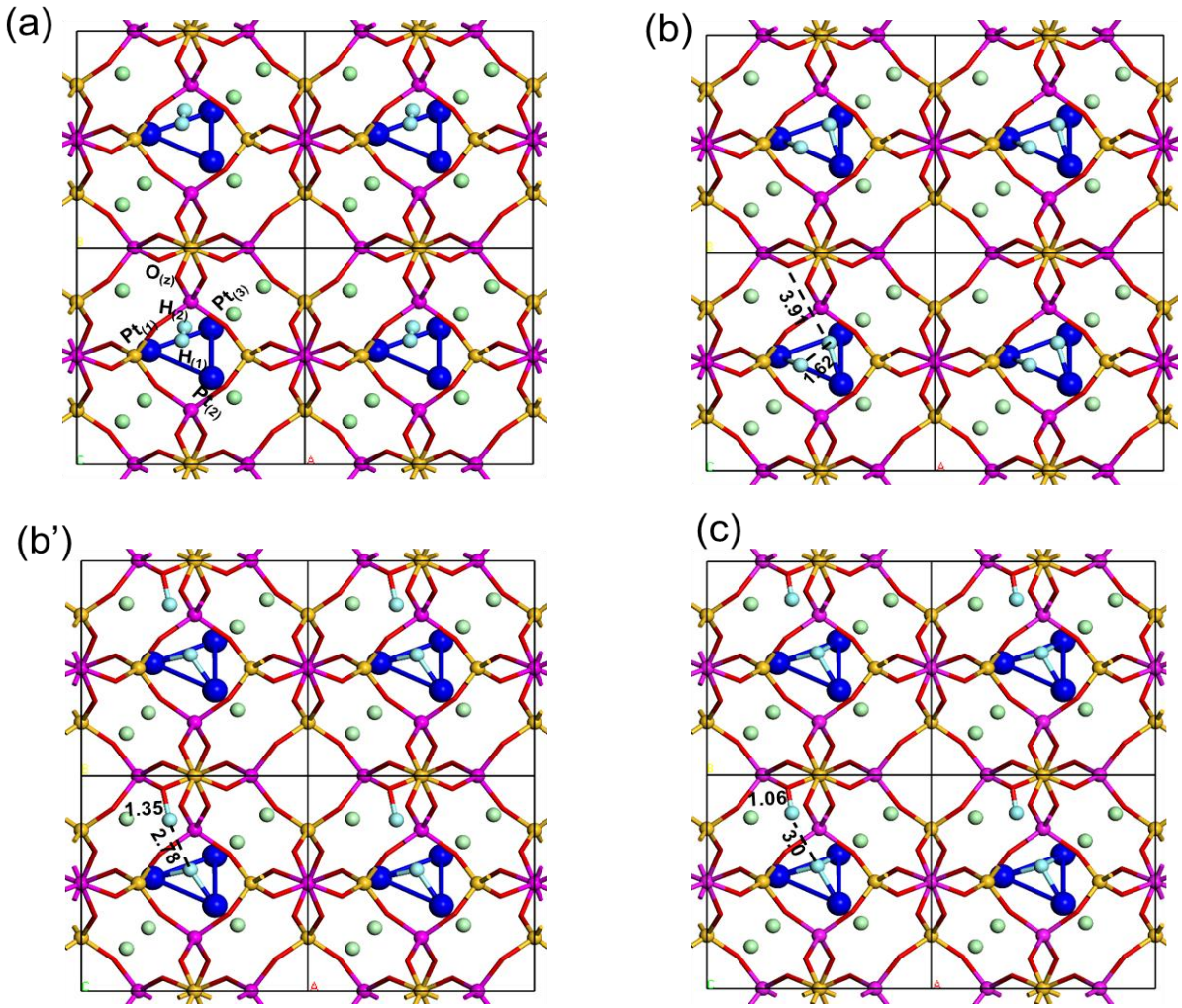
(♦)and NiMo/SiO_2-Al_2O_3 (▲) catalyst (LHSV 1 hr^{-1}, H_2/Liquid feed 2200 (vol./vol.), P=100 bar)

Naphthenes and Aromatics distribution along with H_2 consumption



(C9-C15 range hydrocarbons Pt@SOD-NiMo-SiO_2-Al_2O_3 catalyst (LHSV 1 hr^{-1}, H_2/Liquid feed 2200, P=100 bar) with temperature

Naphthenes and Aromatics distribution along with H_2 consumption



(C9-C15 range hydrocarbons Pt@SOD-NiMo-SiO_2-Al_2O_3 catalyst (LHSV 1 hr^{-1}, H_2/Liquid feed 2200, P=100 bar) with temperature

Comparison of Pt@SOD-NiMo-SiO_2-Al_2O_3 with other catalysts

Catalyst	Temp, °C	Pressure (bar)	H_2/HC	Conv. (%)	Oligomers (>C18) yield%	Time on stream (h)
Pt@SOD-NiMo-ZSM-5	380	80	2000	99.0	9	350
NiMo/SiO_2-Al_2O_3	380	100	2200	99.9	5	600
Pt@SOD-NiMo-SiO_2-Al_2O_3	380	100	2200	99.9	3	660

- Undesirable coke precursors (>C18 oligomers) are nearly 3 times more on Pt@SOD-NiMo(S)-ZSM-5 than the current catalyst.
- Pt@SOD-NiMo-SiO_2-Al_2O_3 shows longer stable activity (660h)
- Higher acidity of ZSM-5 (0.95 $mmol^{-1}$) and mixed micro-mesoporosity (pore sizes: 0.6 nm, 13 nm) compared to mesoporous SiO_2-Al_2O_3 (acidity: 0.77 $mmolg^{-1}$; pore size: 8.6 nm), makes the former more susceptible to deactivation during hydrocracking reaction

Publications

- ✓ **S. A. Farooqui**, M. Anand, A. Khan, R. Kumar, T.S. Khan, M.A. Haider, A.K. Sinha; Noble metal encapsulated sulfide catalyst for the production of aviation biofuel from the hydroprocessing of non-edible oils, **Materials Science for Energy Technologies, Volume 4, 2021, Pages 413-422 September 2021, DOI: 10.1016/j.mset.2021.09.00**

- ✓ **Temperature-dependent reaction pathways for the anomalous hydrocracking of triglycerides in the presence of sulfided Co-Mo-catalyst; Bioresource Technology 126 (2012) 148–155**

- ✓ **Enhanced growth of micro alga Botryococcus braunii using adsorbants; J. Algal Biomass Utln. 2012, 3 (1): 5 – 10**

- ✓ **Jatropha-oil conversion to liquid hydrocarbon fuels using mesoporous titanosilicate supported sulfide catalysts; Catalysis Today Volume 198, Issue 1, 30 December 2012, Pages 314–320**

- ✓ **Aviation fuel production from lipids by a single-step route using hierarchial mesoporous zeolites, Energy and Environmental science, 2011, 4, 1667-1671**

Book Chapter:

Saleem A. Farooqui, Anil K. Sinha, Anjan Ray; Chapter13-Progress and trends in renewable jet fuels; **Advanced Biofuel Technologies, Present Status, Challenges and Future Prospects, 2022, Pages 333-364, https://doi.org/10.1016/B978-0-323-88427-3.00011-8**

Farooqui, S.A., Kumar, R., Sinha, A.K., Ray, A. (2022). Green Diesel Production by Hydroprocessing Technology. In: Aslam, M., Shivaji Maktedar, S., Sarma, A.K; **Green Diesel: An Alternative to Biodiesel and Petrodiesel. Advances in Sustainability Science and Technology. Springer, Singapore https://doi.org/10.1007/978-981-19-2235-0**

Thank You

Biofuels Team

CSIR-Indian Institute of Petroleum, Dehradun

Domestic Carbon Sources

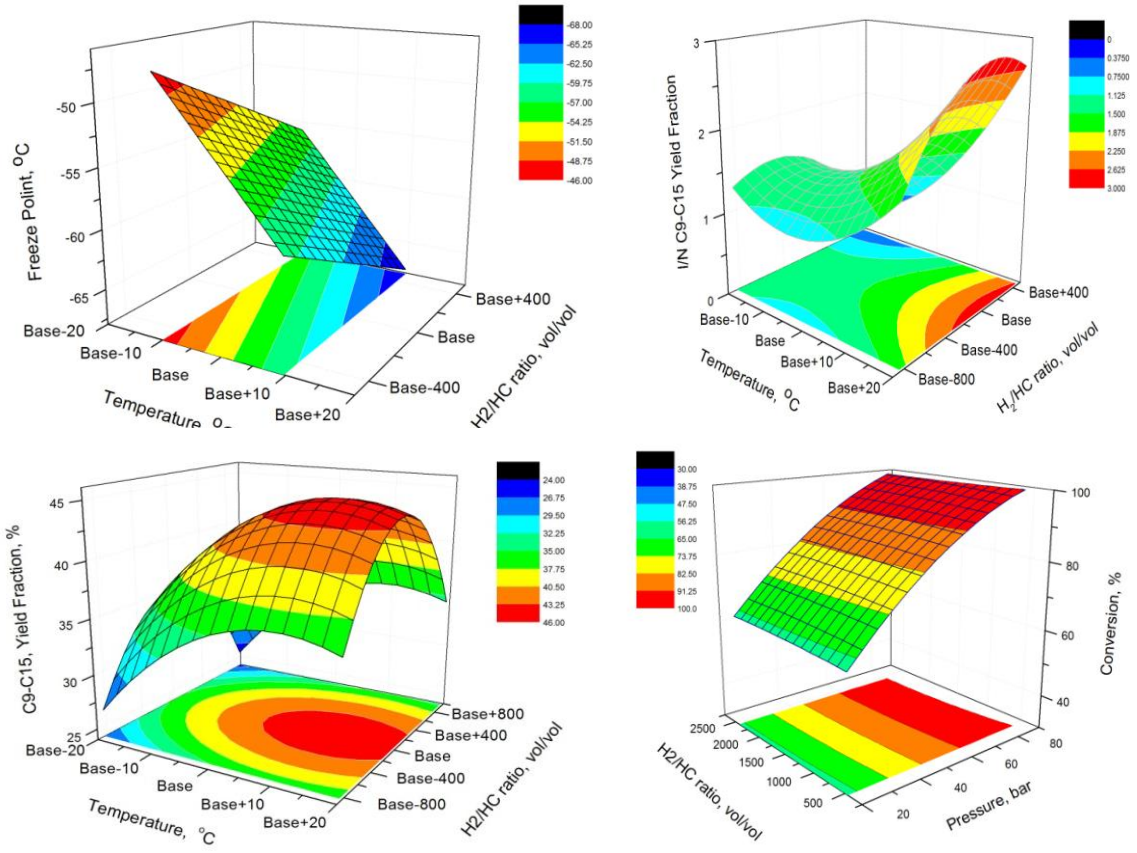
- **Used Cooking oil**
  - Estimated ~2 million tons annually @ 10% of total edible oil consumed in India
  - As of today, simply goes “down the drain” and adds to environmental burden
  - China collects and trades over 1 MM TPA already of its domestic UCO
  - Easy to access from cantonments, canteens, community kitchens
- **Tree borne oils**
  - Over 400 species identified in India, growing wild
  - Lack of demand and no incentives for collection of seeds limits supply side
- **Short rotation crops**
  - Non-edible oilseeds like niger, carinata, camelina etc (mustard family)
  - Can be planted and grown between staples as a second or third crop
  - Need organized long term demand to stimulate farmer interest

“Annually, about 23-million tonne cooking oil is consumed in India. There is potential to recover and use about 3 million tonnes of this after cooking,” FSSAI

As of now, used cooking oil is either not disposed in an environmentally hazardous manner and sometimes even finds it way to smaller restaurants, *dhaabas* and street-vendors.

https://www.thehindubusinessline.com/economy/policy/new-regulations-for-used-cooking-oil-come-into-effect/article24314377.ece

Effect Feed/Process Condition on Product yields



Sulfided Ni-Mo - hierarchical mesoporous H-ZSM-5 high yield of jet fuel from jatropha and algal oil

Variation of mean i/n ratios for C9-C14 fraction

Catalyst	H_2/Feed, Nl/L (1500)	H_2/Feed, Nl/L (2200)
NiMo-7	3.0	3.8
NiMo-11	1.6	3.95[a]
NiMo-15	3.9	-

420 ℃, 1hr-1, 80 bar. (a: 400 ℃)

Catalyst	LHSV of 1 h^{-1}	LHSV of 2 h^{-1}
NiMo-7	3.8	3.1
NiMo-11	3.95[a]	2.7
NiMo-15	-	4.46

420 ℃, 80 bar. (a: 400 0C), H_2/HC 2200 Nl/L

The increased H_2/feed ratios increase the free hydrogen availability on the active metal sites, promoting isomerization reactions. Adequate acidity was available in all three catalysts for the isomerization reactions.

Effect of unsaturation in the feed on hydroconversion reaction over NiMo /SiO_2-Al_2O_3 and hydrodynamic simulation of the reactor to control exothermicity

Composition of different feeds used in pilot plant

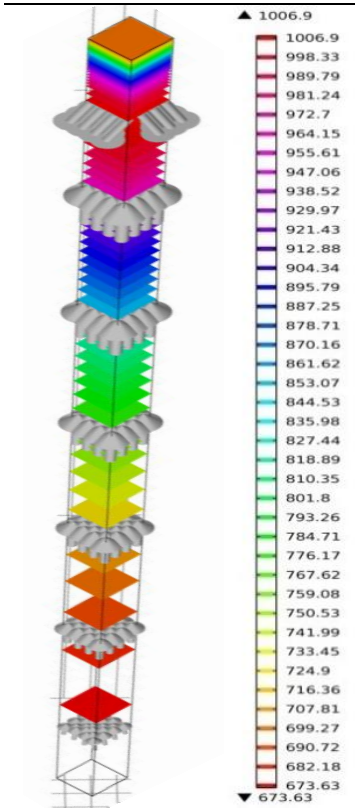
	Used cooking Oil	Jatropha	Pongamia	Palm stearin	PFAD
Palmitic acid ($C_{16:0}$)				49.8-69.1	48.9
Linolenic acid ($C_{18:3}$)	1-3		2.6	0.1-0.5	
Linoleic acid ($C_{18:2}$)	13	41.7	16.0	5.0-8.9	9.7
Oleic acid ($C_{18:1}$)	70	41.8	51.5	20.4-34.4	37.4
Saturated fatty acids	16	16.5	29.9	~75.7	52.7
Unsaturation	83.2	**83.5**	70.1	**~24.3**	47.3

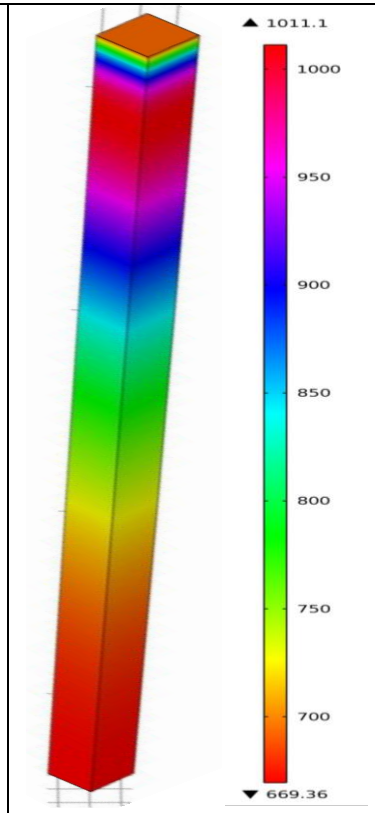
1. Nagaraj and Mukta (2004)
2. Biodiesel Production using Karanja and Jatropha seed Oil; *Lekha Charan Meher, Satya Narayan Naik,Malaya Kumar Naik, and Ajay Kumar Dalai;* Handbook of Plant-Based Biofuels
3. Variation of the Chemical Composition of Waste cooking Oils upon Bentonite Filtration; Alberto Mannu et. al. Resources 2019, 8, 108

Temperature profile-No Quench (Simulated)

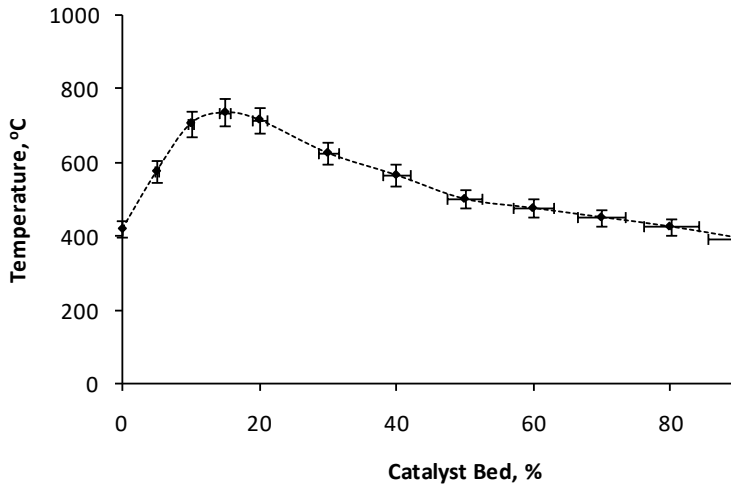
Creating Future Fuels

Temperature Gradients (K)



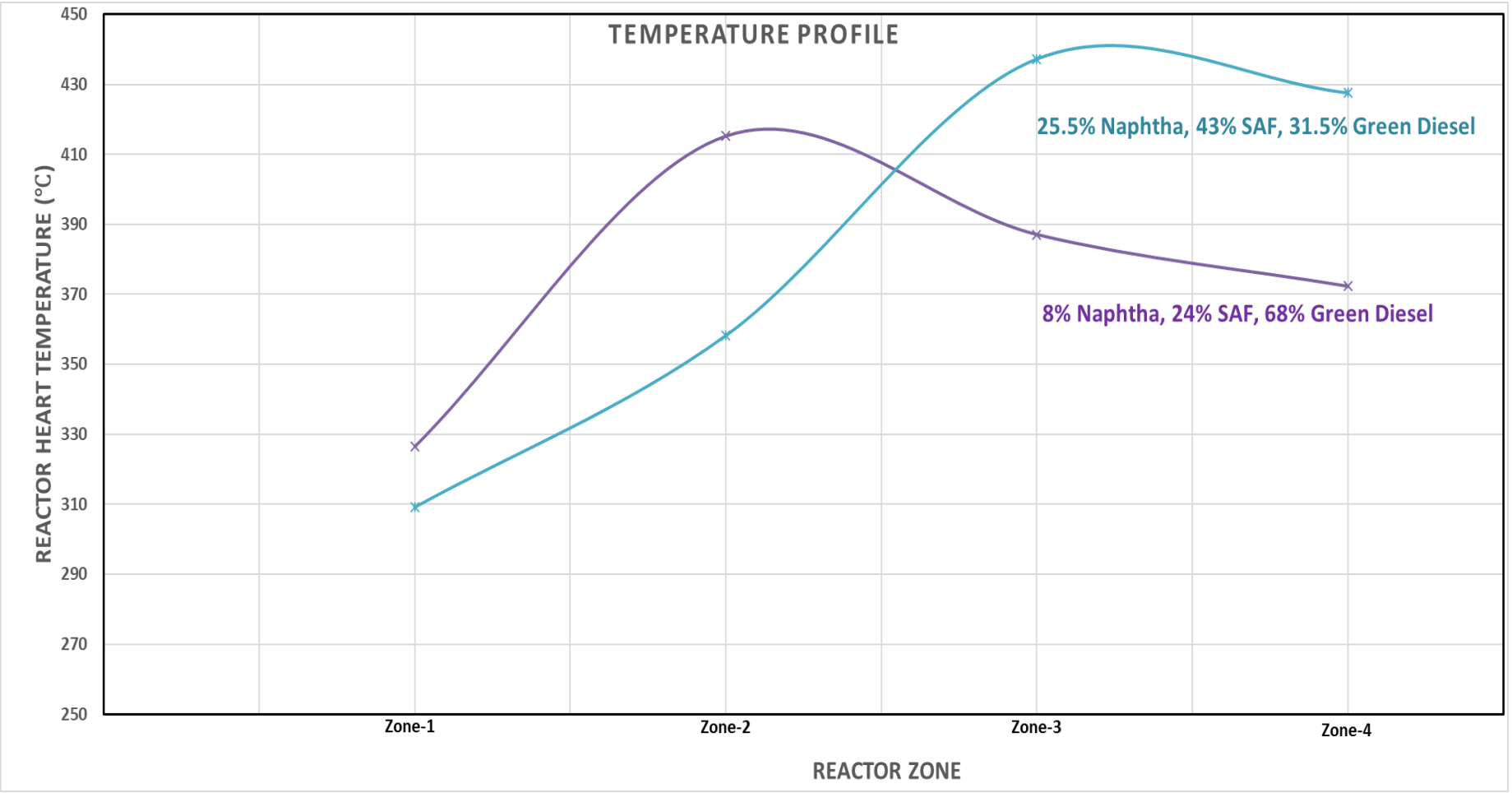


Bed Temperature Profile (C)



Reactor temperature profile-Pilot plant data

Creating Future Fuels

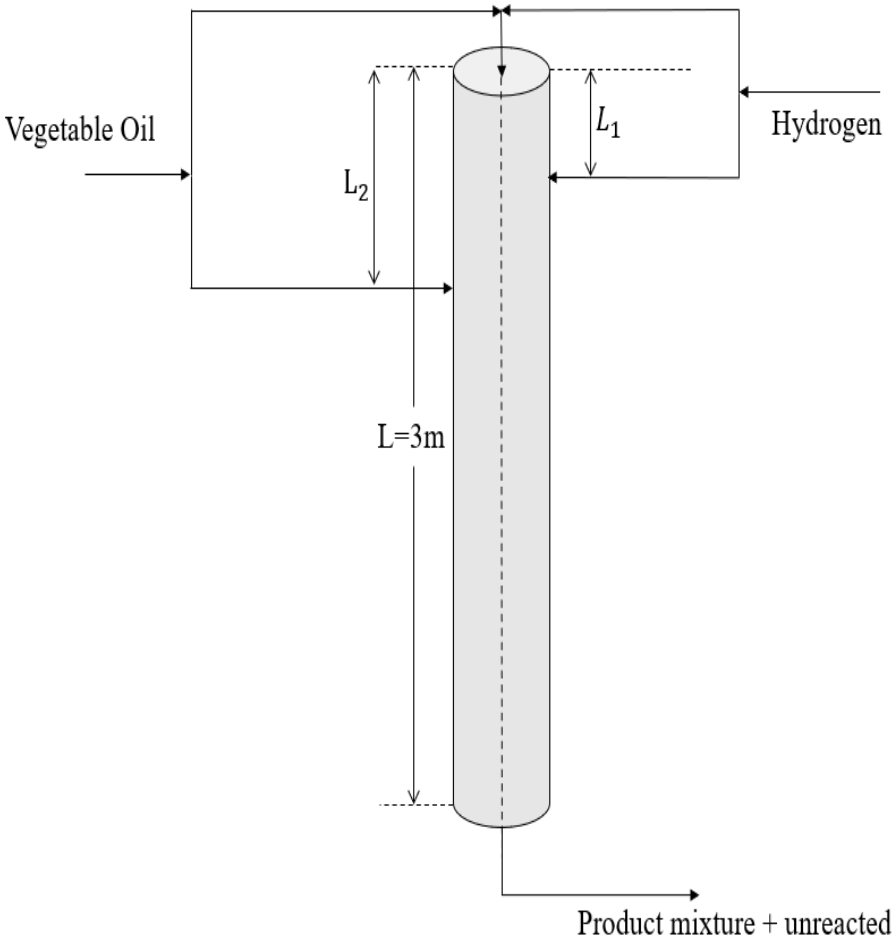


Heats of reactions for the major reactions, during the hydroprocessing of lipids

Reaction $\Delta H_r^o = \sum \Delta H_{fProducts}^o - \sum \Delta H_{fReactants}^o$	, MJ/mole
Depropanation $C_{57}H_{110}O_6(v) + 3H_2(g) \xrightarrow{\Delta\ Catalyst} C_3H_8(g) + 3C_{18}H_{36}O_2(v)$	-1.02
Decarboxylation $C_{18}H_{36}O_2(v) \xrightarrow{\Delta\ Catalyst} CO_2(g) + C_{17}H_{36}(v)$	+0.03
Decarbonylation $C_{18}H_{36}O_2(v) + H_2(g) \xrightarrow{\Delta\ Catalyst} CO(g) + H_2O(v) + C_{17}H_{36}(v)$	+0.07
Hydrodeoxygenation $C_{18}H_{36}O_2(v) + 3H_2(g) \xrightarrow{\Delta\ Catalyst} C_{18}H_{38}(v) + 2H_2O(v)$	-0.079
Hydrocracking $C_{18}H_{38} + H_2 \xrightarrow{\Delta} C_{12}H_{26} + C_6H_{14} \quad \Delta H_{r\,C_{18}H_{38}}^o = -0.04247 MJ/mole$	-0.04
Hydrocracking $C_{17}H_{36} + H_2 \xrightarrow{\Delta} C_8H_{18} + C_9H_{20} \quad \Delta H_{r\,C_{17}H_{36}}^o = -0.043 MJ/mole$	-0.04
Hydrogenation of 1 double bond	-0.13

Overall Exothermicity ---→-1.782838734 MJ/kg of feed for Jatropha Oil

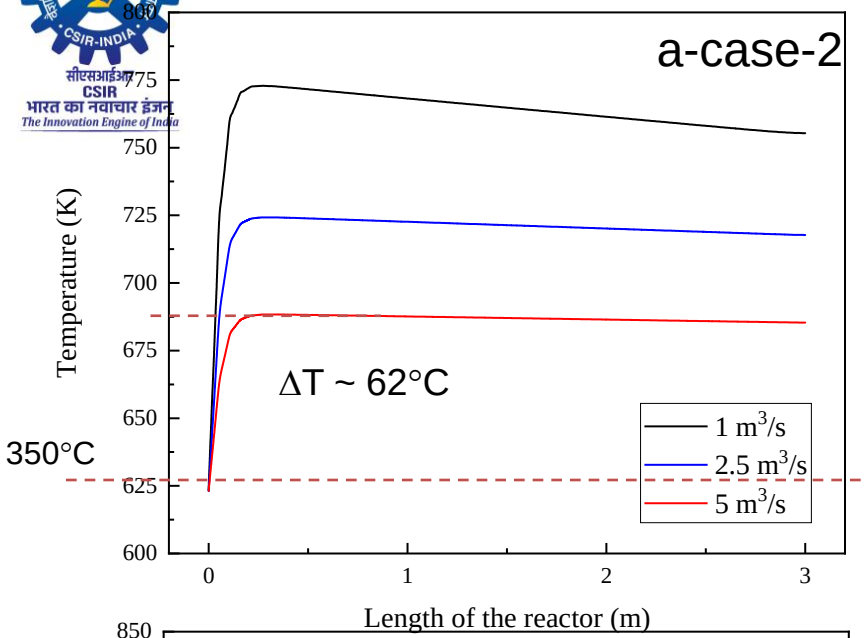
Kinetic data and scheme followed for simulation

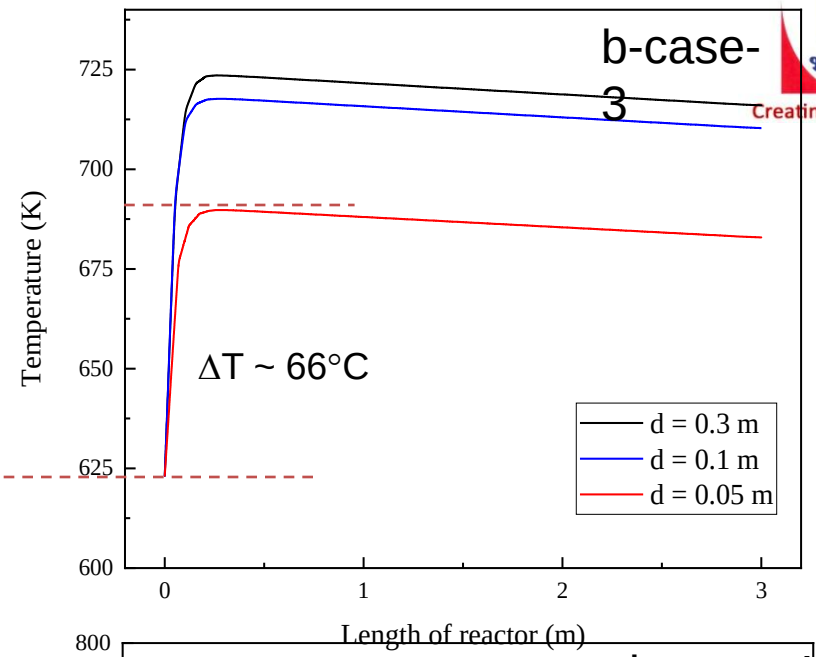


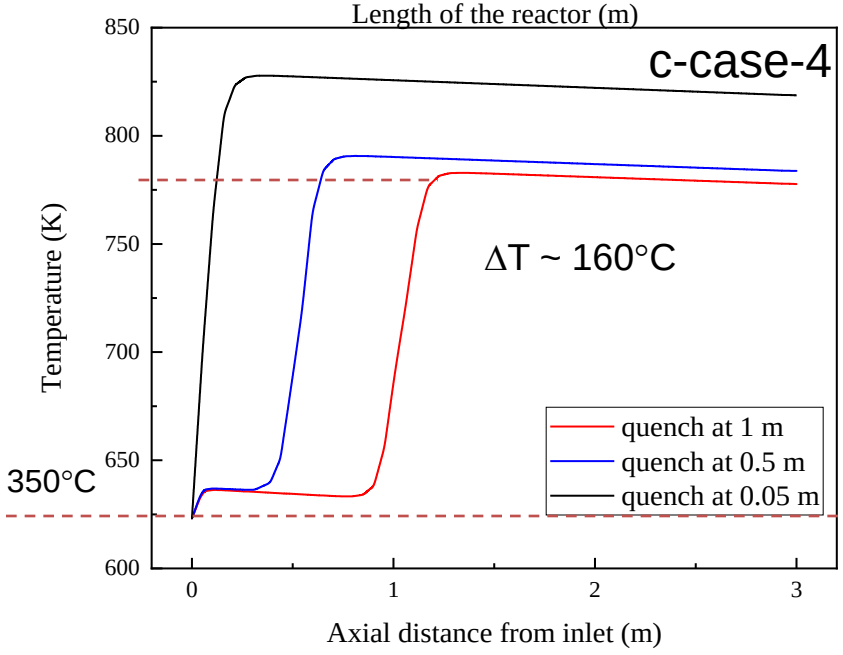
Reaction	Value (hr^{-1})
Vegetable oil → Naphtha	0.6
Vegetable oil → Kerosene	1.2
Vegetable oil → Diesel	18.8
Vegetable oil → Oligomers	2.7
Diesel → Kerosene	0.2
Kerosene → Naphtha	0.1
Diesel → Naphtha	0.1

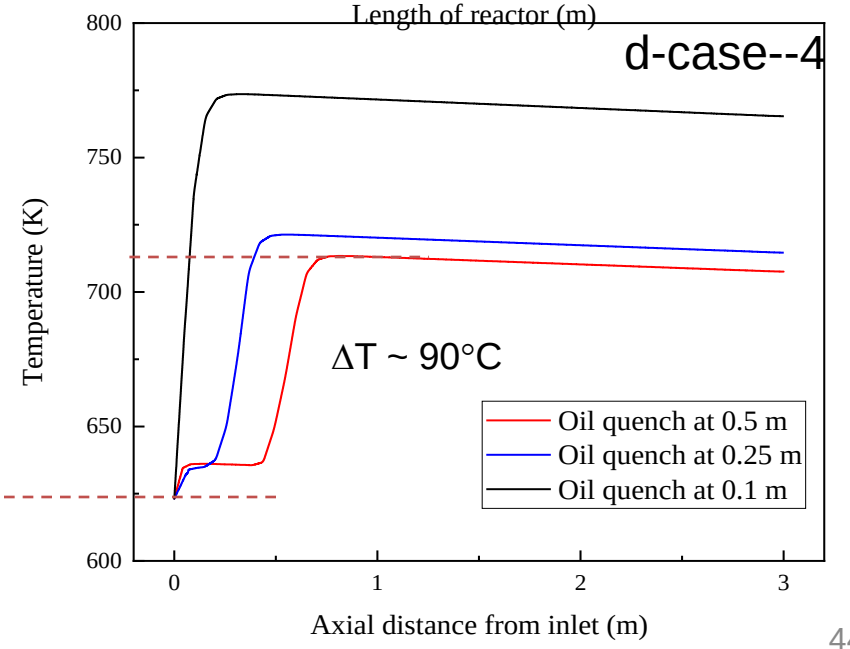
Temperature-dependent reaction pathways for the anomalous hydrocracking of triglycerides in the presence of sulfided Co–Mo-catalyst, Bioresource Technology, Volume 126, December 2012, Pages 148-155

Temperature profile with different quench schemes



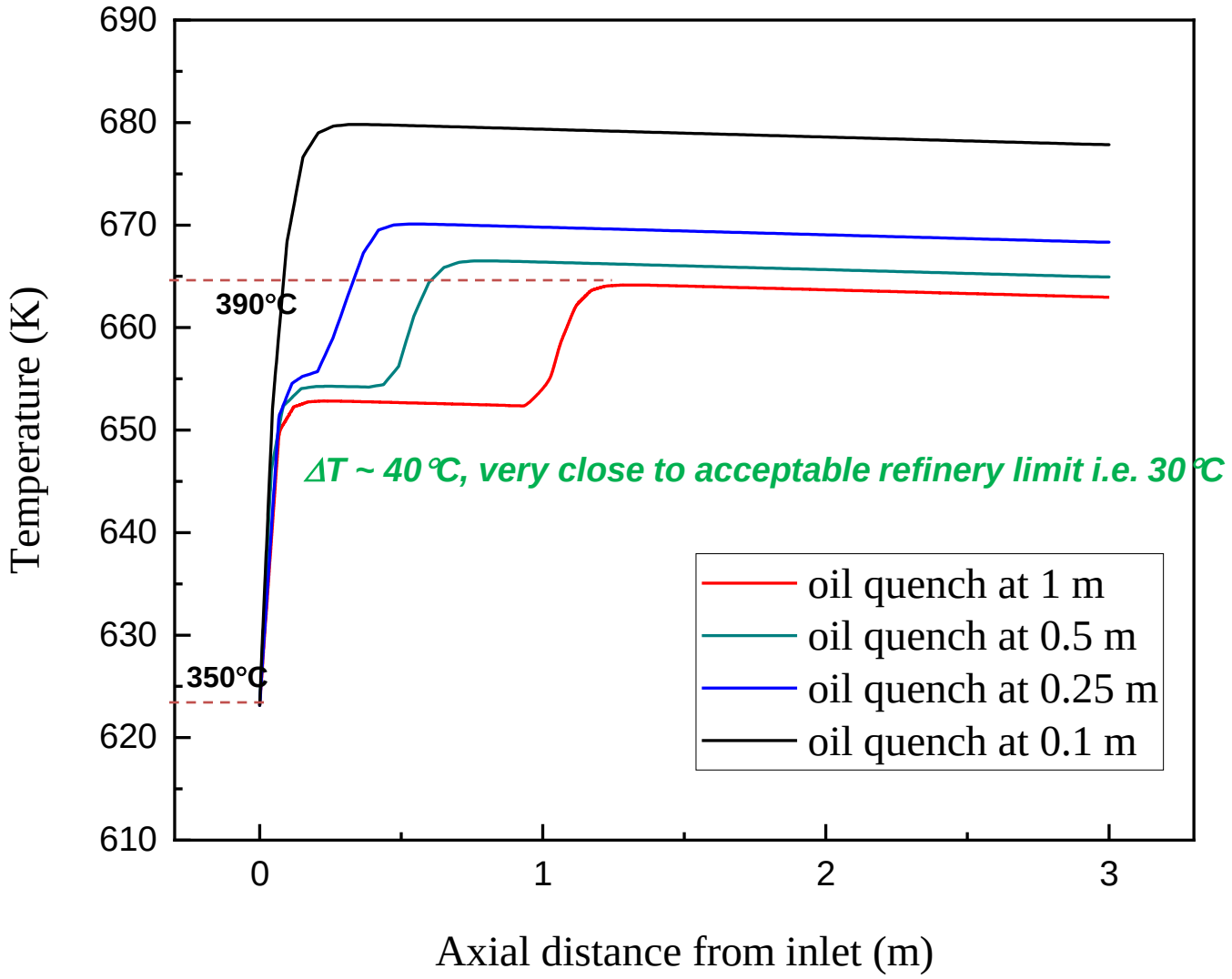






a) H_2 quench flow rate, b) Quench distance-d c) quench H_2 and liquid d) H_2 at d=0.05 with 50% liquid

Best scheme for lowest ΔT across the reactor



Case-5, hydrogen is sent through its optimum quench point (0.05 m from inlet) and vegetable oil (20%) from different quench points

Catalyst development for reduced hydrogen consumption

Conventional Catalysts

H_2 Consumption

Novel Catalysts

H_2 Production

- **Increase in Naphthenes /1R and 2R - Aromatics**