Business from technology

Upgrading of fatty acid containing rosin acids in to high value hydrocarbons via catalytic hydrodeoxygenation

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Why Biomass??

- **Depletion of world wide petroleum resources**
- **Strong environmental concerns about fossil fuels**
- **Biomass is renewable and a rich source of carbon**
- **Easy adaptability with the existing petrorefinery**

It is not enough with renewable but it must also be sustainable!!

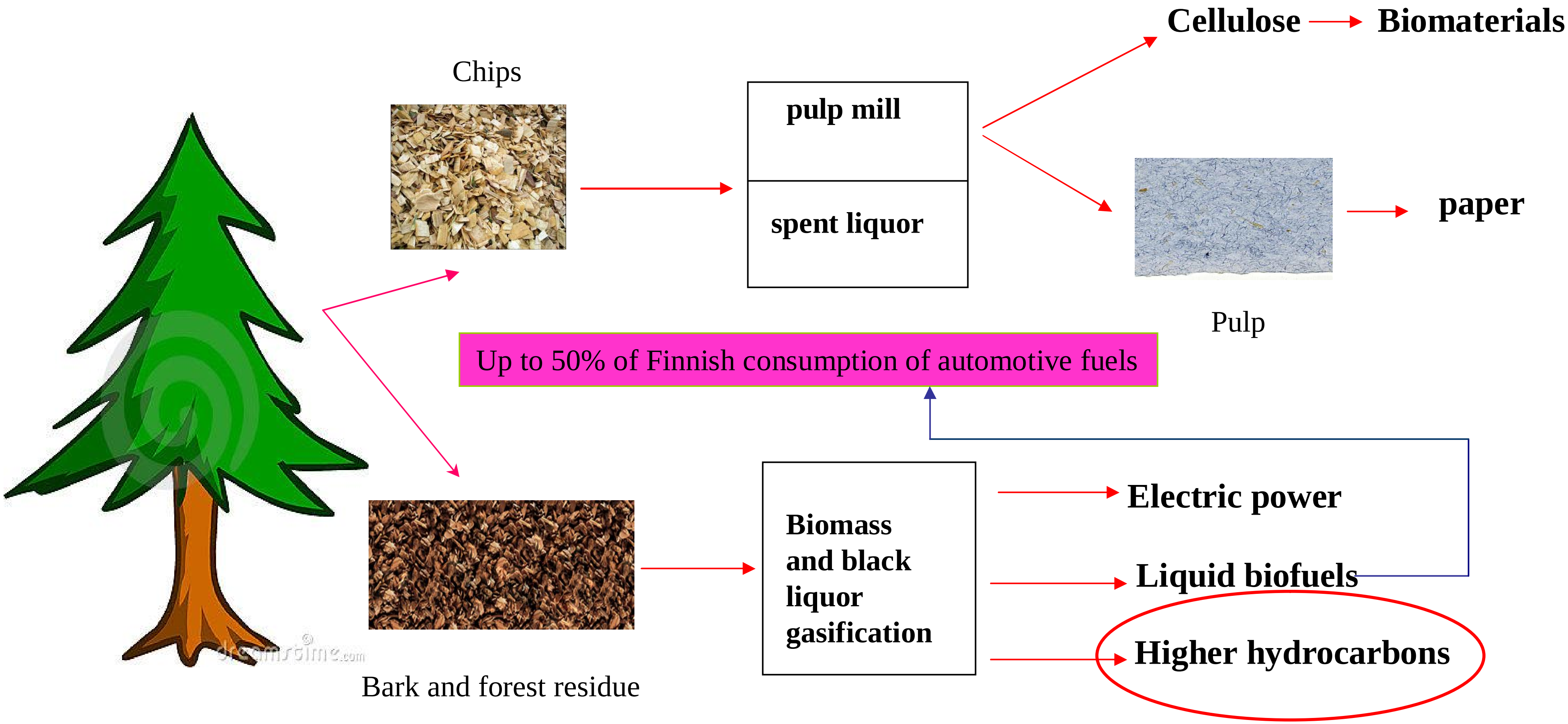
Forest Biorefinery

- **In Finland biorefineries benefit mainly from woody biomass**

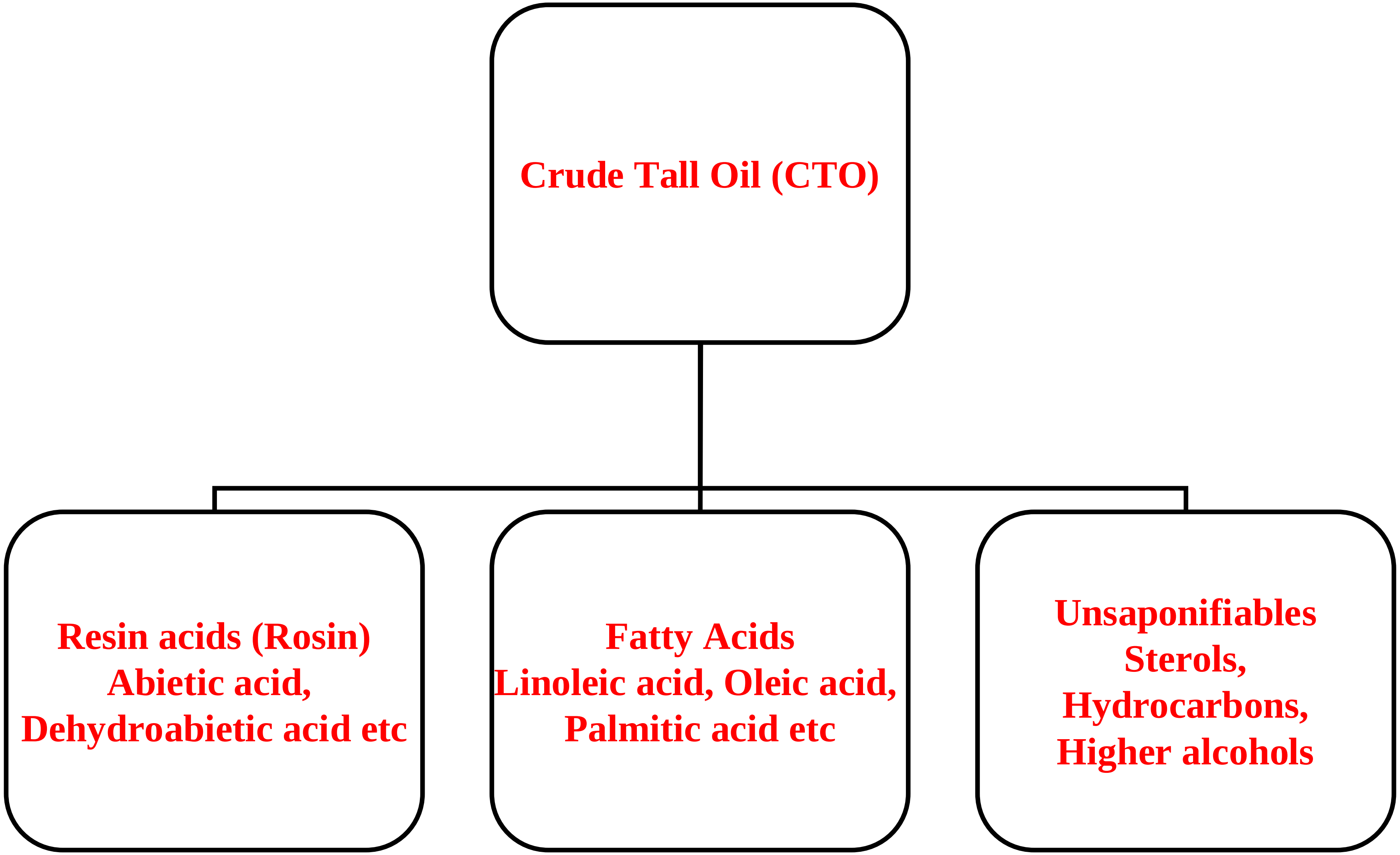
Valuable raw matierals from woody biomass

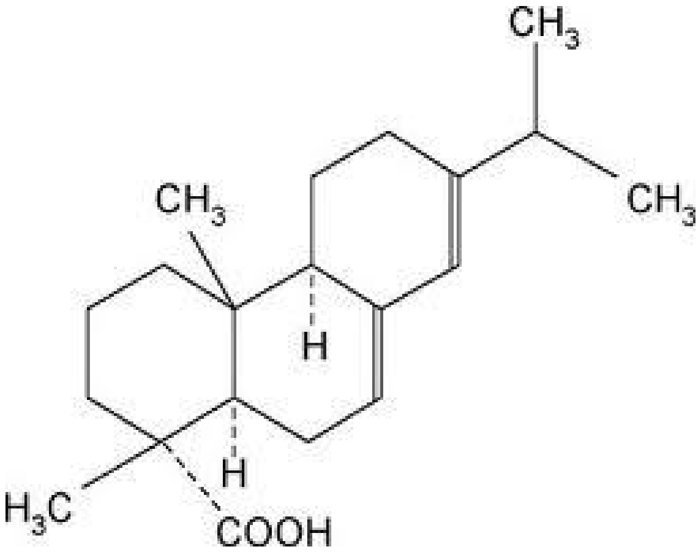
Upgrading of Kraft pulping process in to a multi-product biorefinery concept

Pulp mill biorefinery

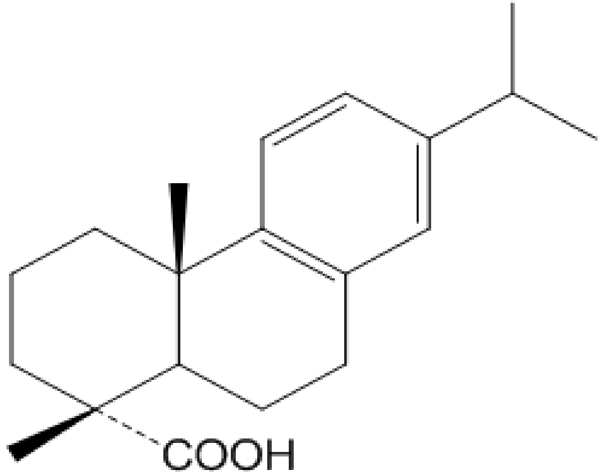


Tall oil, the by-product of paper production meets the criteria of an economically desirable and readily available feedstock

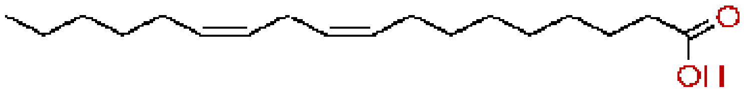

Crude Tall Oil (CTO)
Resin acids (Rosin)
Abietic acid,
Dehydroabietic acid etc
Fatty Acids
Linoleic acid, Oleic acid,
Palmitic acid etc
Unsaponifiables
Sterols,
Hydrocarbons,
Higher alcohols



Abietic acid



Dehydroabietic acid



Linoleic acid

Oleic acid

Chemical Approach

Converting Tall oil fractions in to value added chemicals

Step 1: Upgrading process (to reduce the amount of oxygenates)

Step 2: Catalytic cracking (to produce value added chemicals)

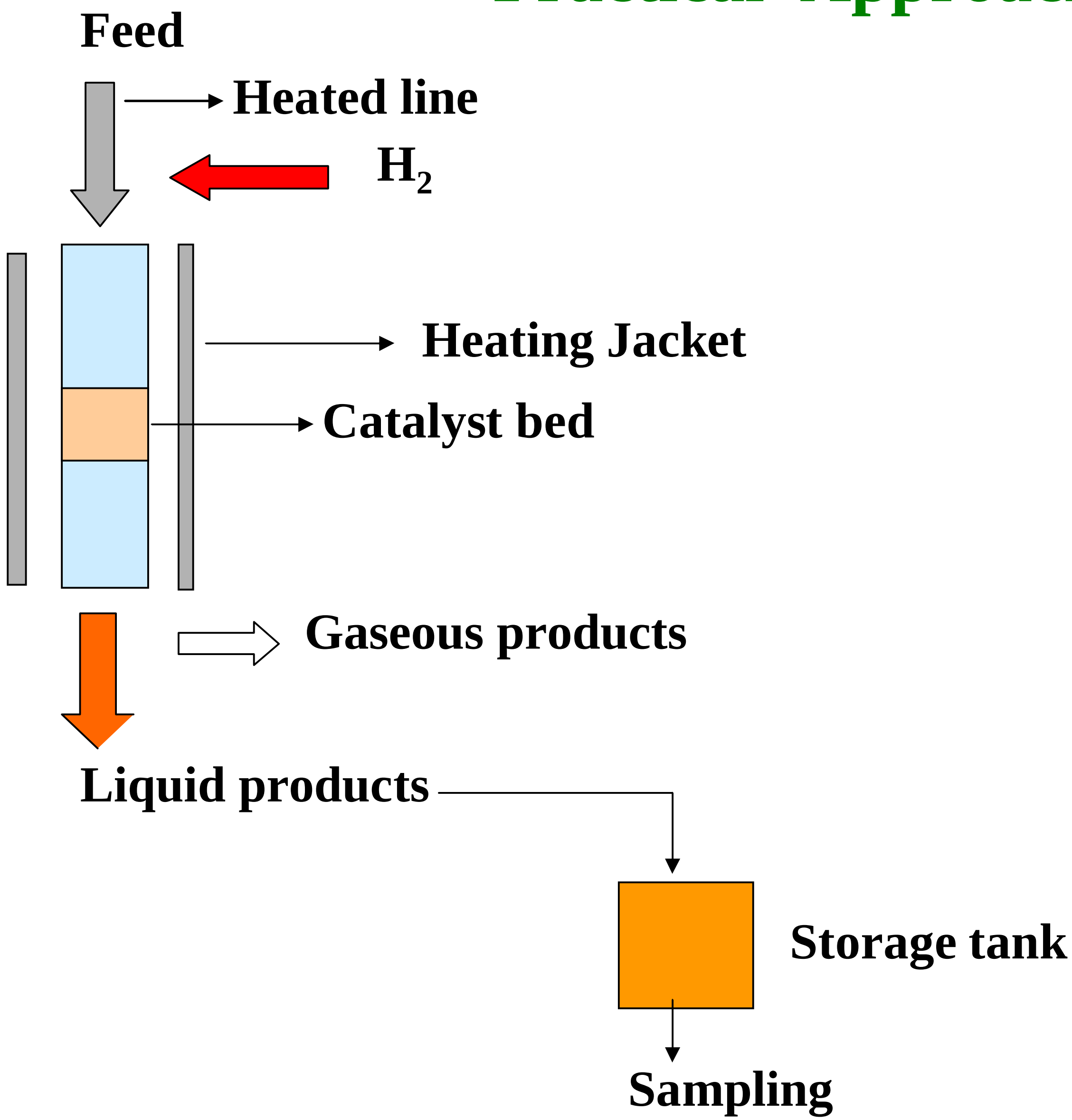
Upgrading!!!!

Hydrodeoxygenation

Hydrodeoxygenation (HDO)

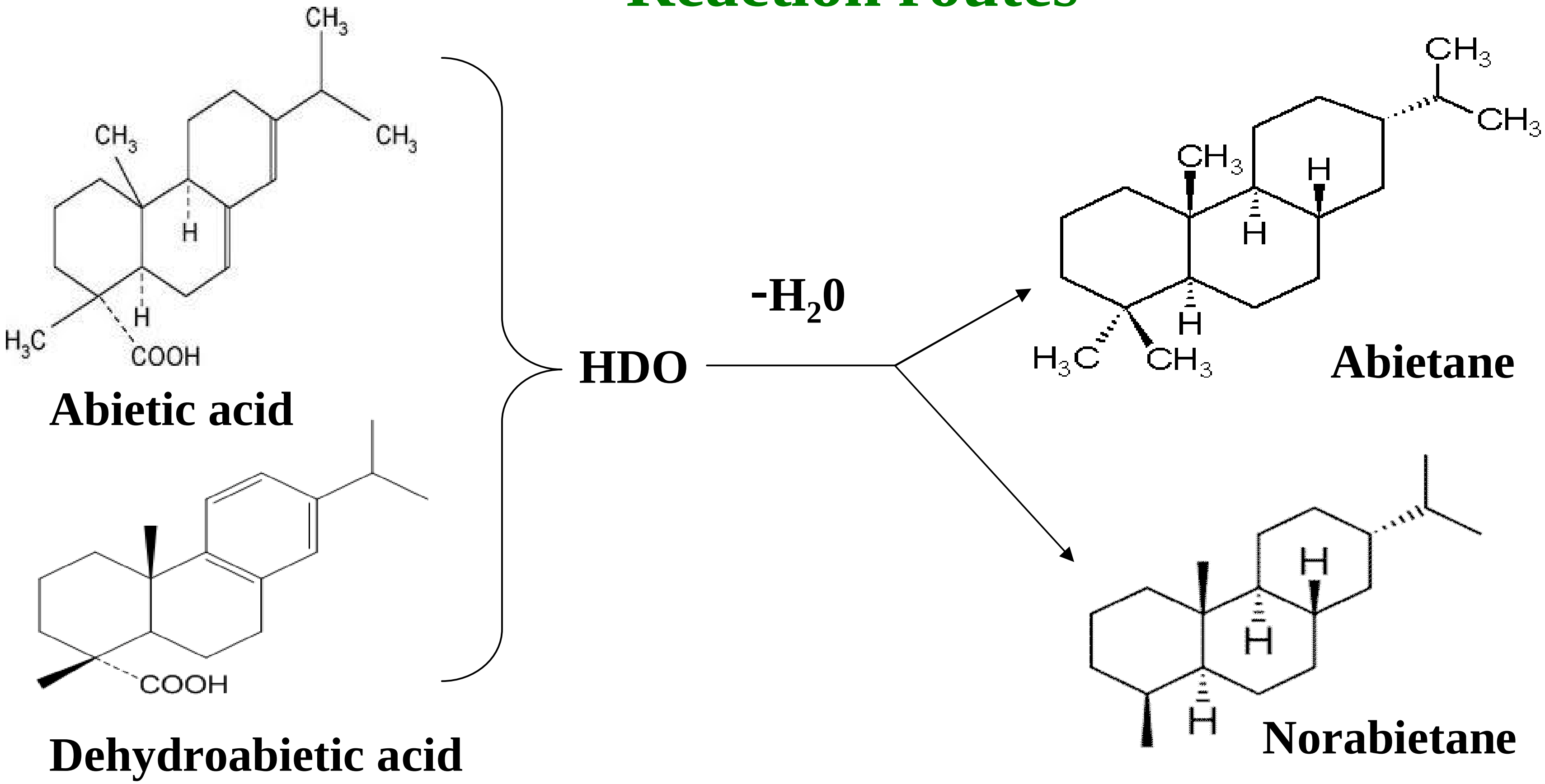
- Removing (or) altering of oxygenated compounds in bio-oil by using hydrotreating catalyst in the presence of hydrogen atmosphere
- Generally oxygenated compounds removed in the form of water mostly
- Hydrotreating catalysts used at present
  - Zeolites (HZSM-5,SUZ-4 etc)
  - Nickel-Molybdenum over γ alumina (NiMo/ γ alumina)
  - Cobalt-Molybdenum over γ alumina (CoMo/ γ alumina)
  - Precious metal catalysts

Practical Approach



- Reactor packing
  - **NiMo (commercial)**
  - Pressure test (40-50 bar) with N2 or Ar
- Presulphidation
  - 5 hrs @ 400 °C (450 °C)
  - H2S/H2 = 5.5 %
- Experiment conditions
  - H2/ Feed = WHSV= 1,1.5 and 2
  - T = 325 °C- **450 °C**
  - Pressure =50 bar (H2)
  - t = 6 hrs

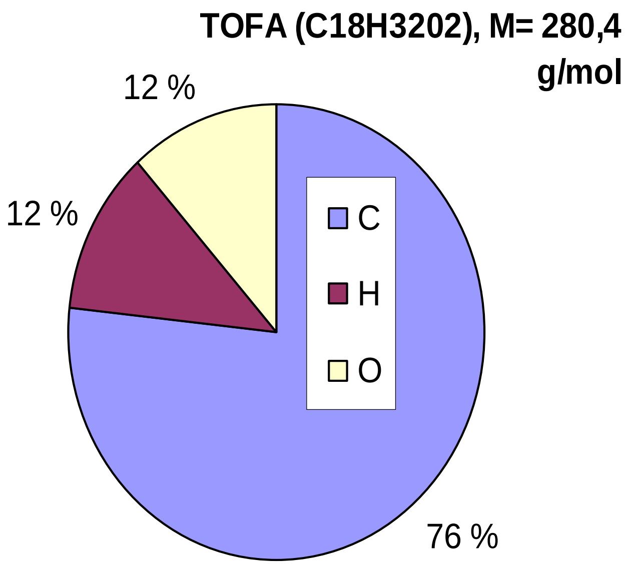
Reaction routes

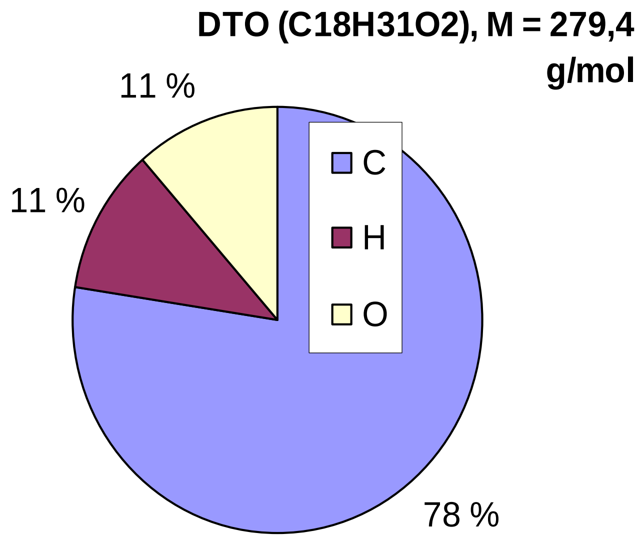


Linoleic acid **HDO** **Oleic acid**

n-Octadecane

Tall Oil Fatty Acid (TOFA) and Distilled Tall Oil composition

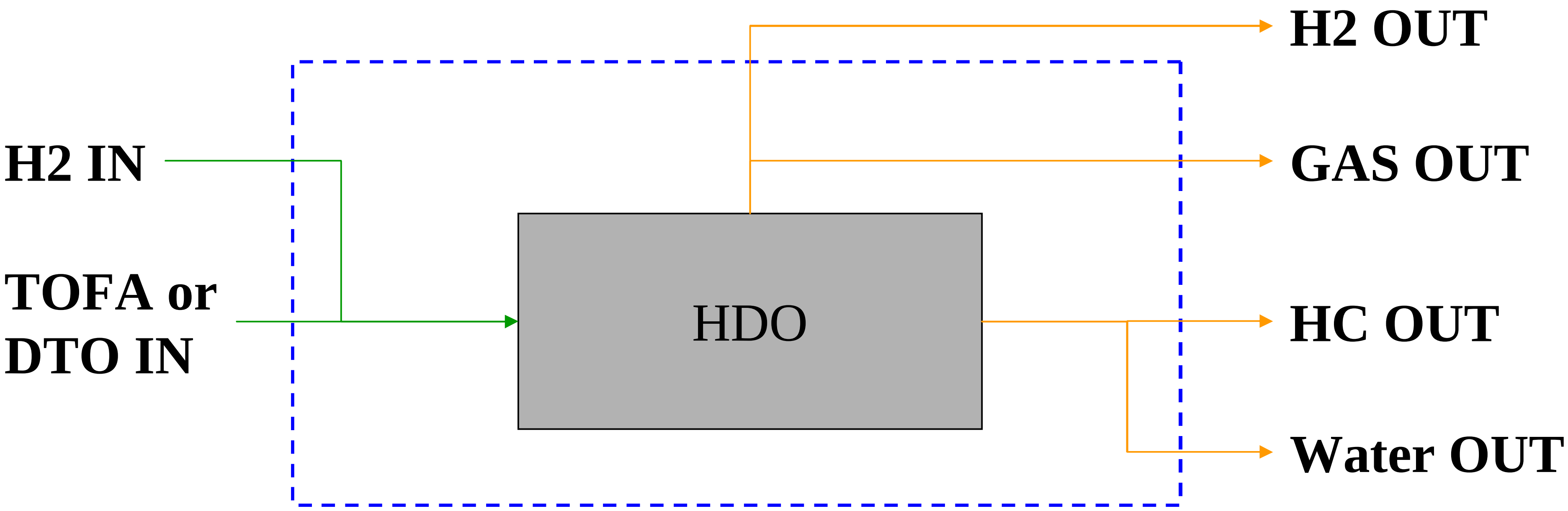




Free fattyacids: 96%
Free rosin acids: 1.8%

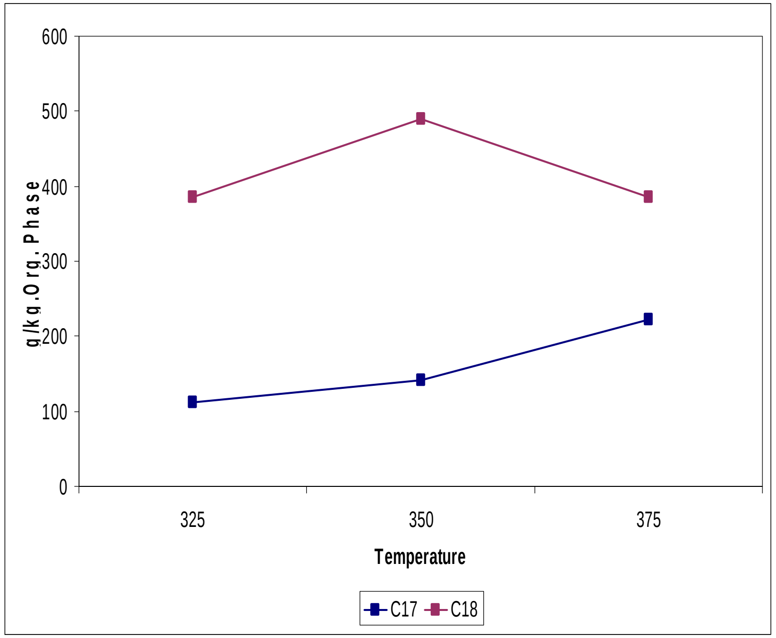
Free fattyacids:70%
Free rosinacids:27%

Mass balance estimation

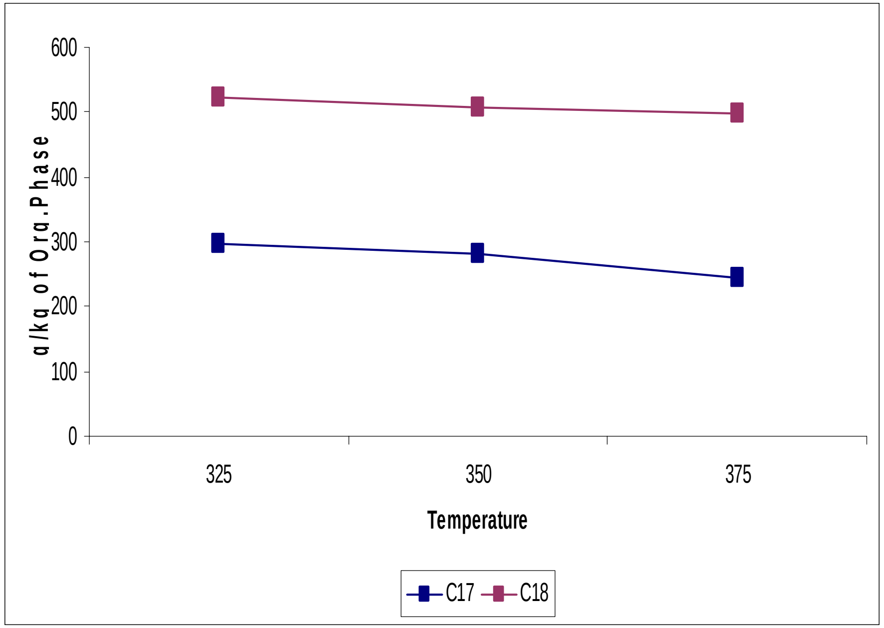


HC analysis : GC-MS and GCXGC
Water analysis: Karl-Fisher titration
Gas analysis: GC and FT-IR
Elemental analysis

HDO of TOFA



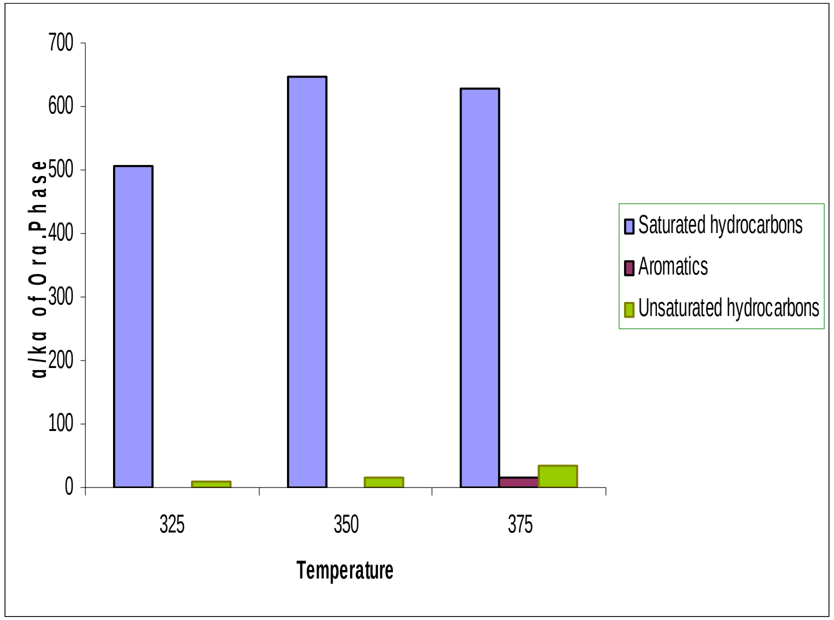
HDO product yields: HDO Vs Decarboxylation
Feedstock: TOFA, T = 325-375º C, Pr: 50bars,WHSV: 2h^{-1}



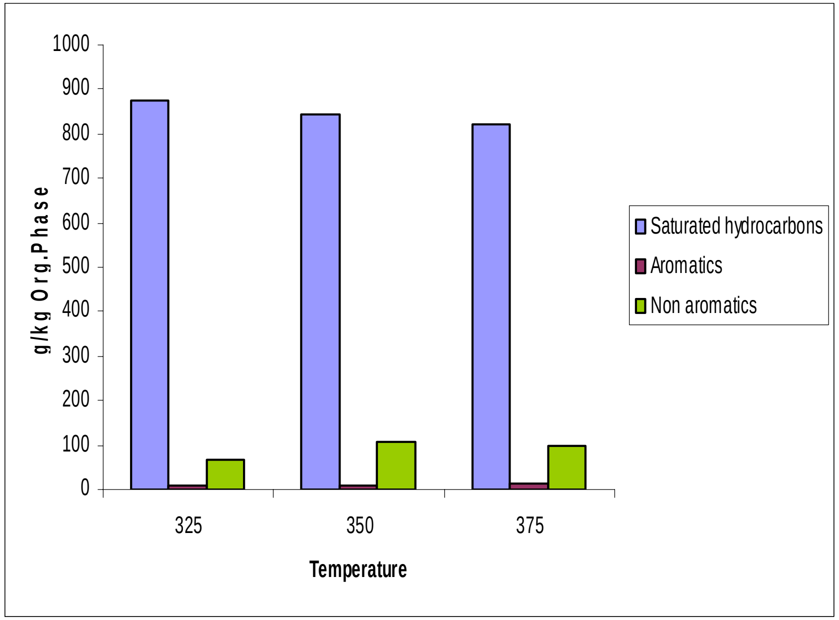
HDO product yields: HDO Vs Decarboxylation
Feedstock: TOFA, T = 325-375º C, Pr: 50bars,WHSV: 1.5 h-1

Steady state HDO activity with increase of temperature at longer residence time

HDO of TOFA



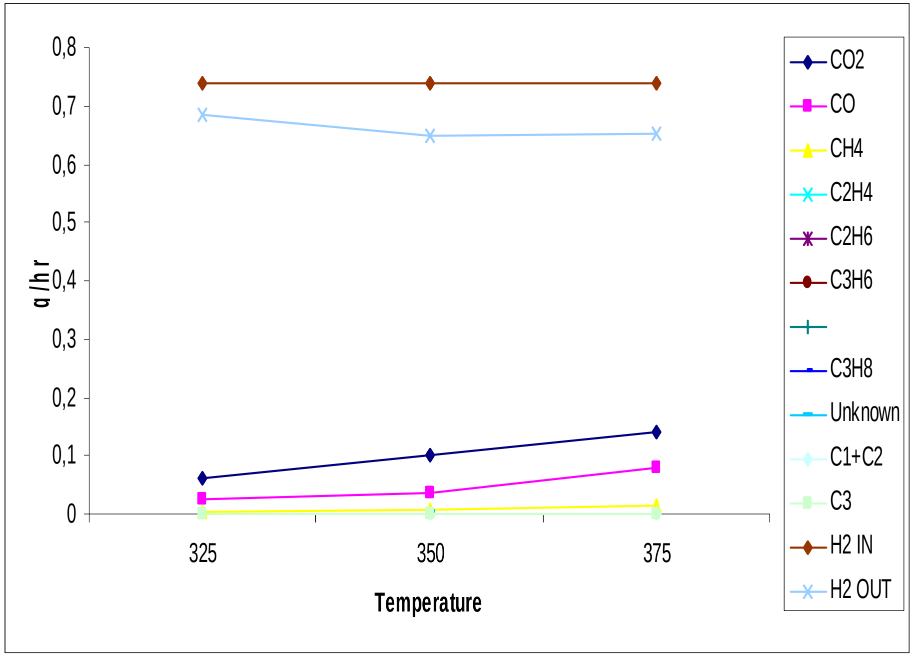
Product distribution: Saturated HC Vs Aromatics
Feedstock: TOFA, T = 325-375º C, Pr: 50bars,WHSV: 2h^{-1}



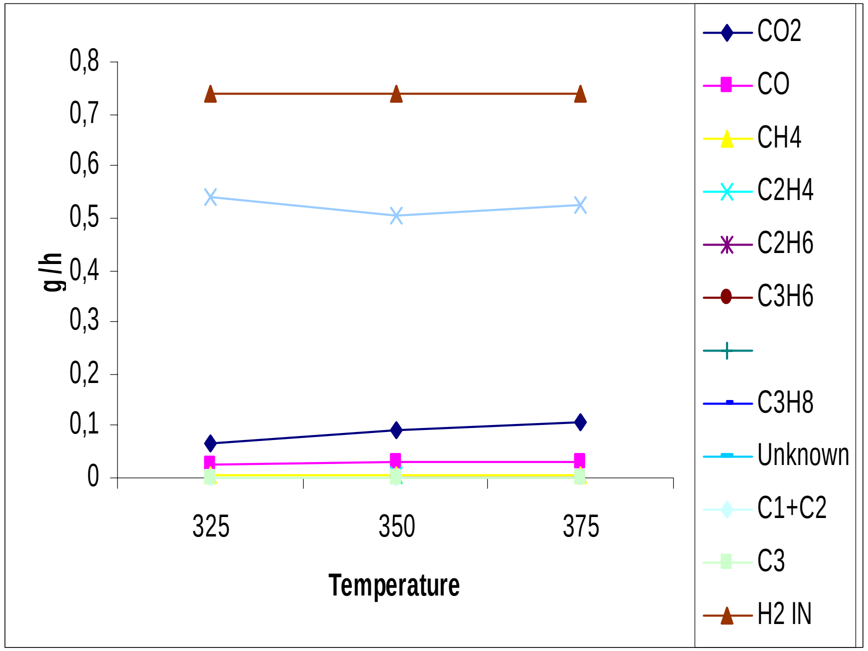
Product distribution: Saturated HC Vs Aromatics
Feedstock: TOFA, T = 325-375º C, Pr: 50bars,WHSV: 1.5h^{-1}

Aromatics appear only at higher temperature
More aromatics at longer residence time

HDO of TOFA



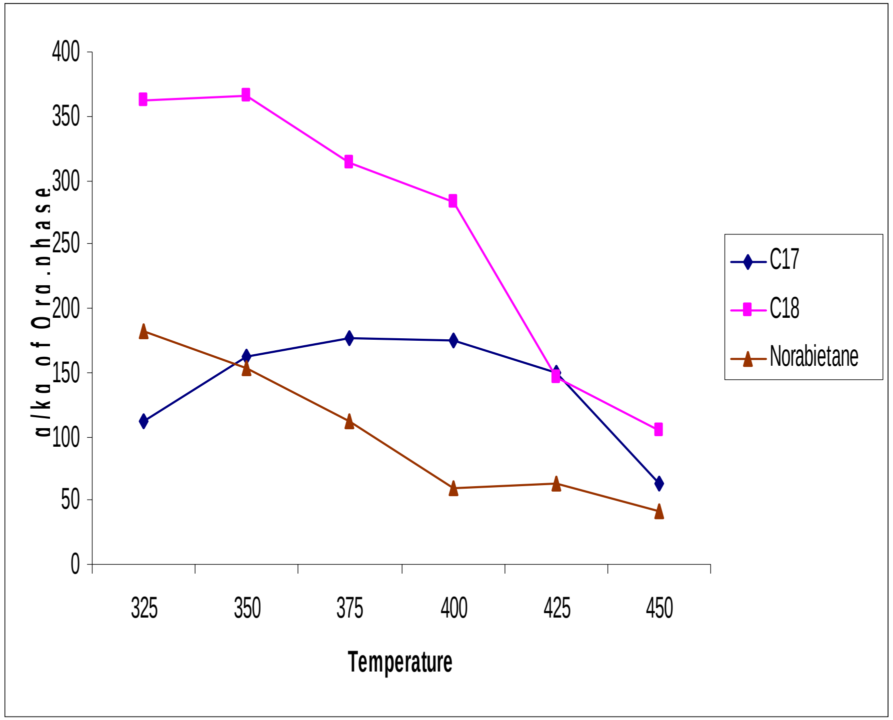
Gaseous products distribution
Feedstock: TOFA, T = 325-375º C, Pr: 50bars,WHSV: 2h-1



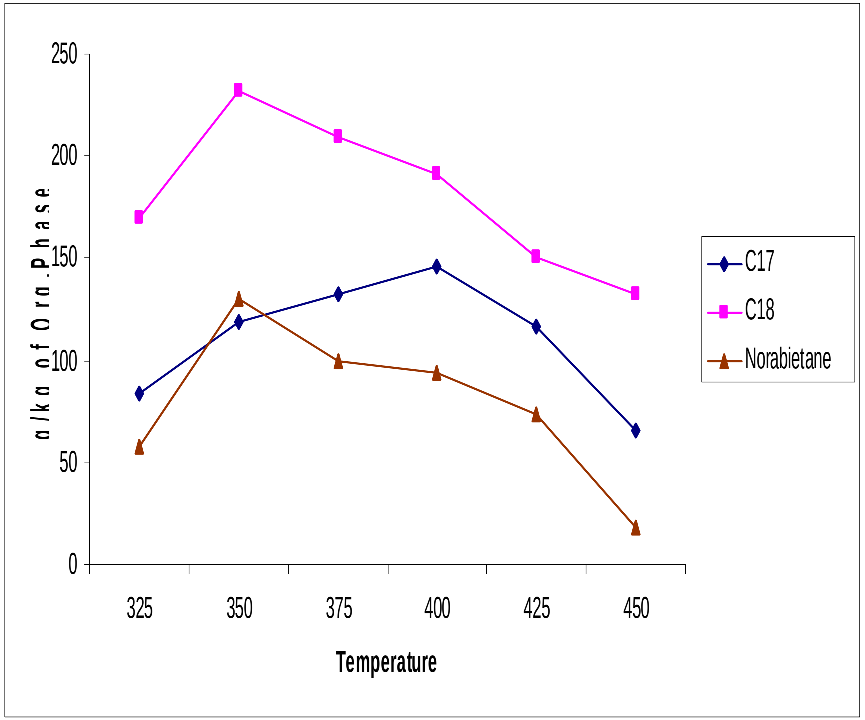
Gaseous products distribution
Feedstock: TOFA, T = 325-375º C, Pr: 50bars,WHSV: 1.5h^{-1}

Reduced decarboxylation rate at longer residence time

HDO of DTO



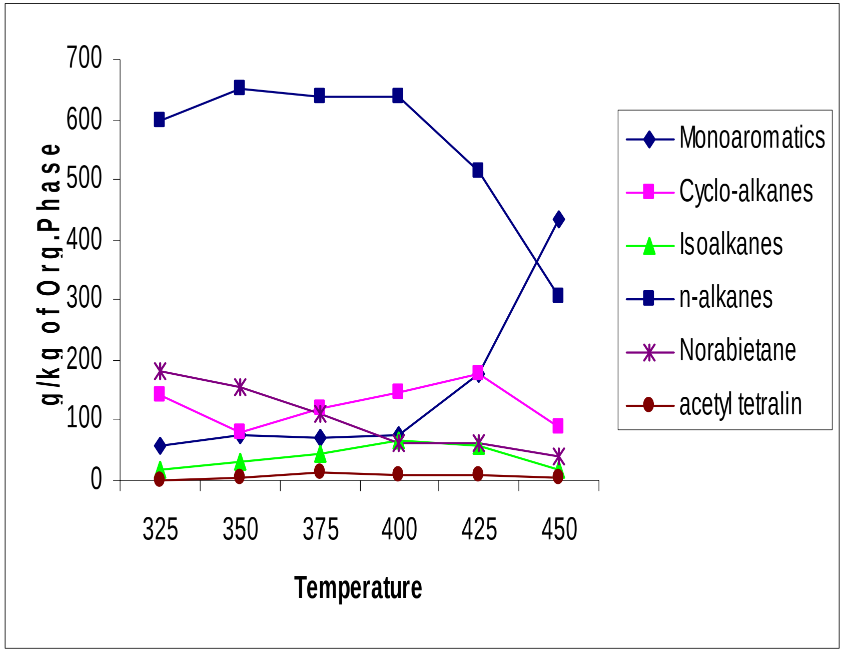
HDO product yields: HDO Vs Decarboxylation
Feedstock: DTO, T = 325-450º C, Pr: 50bars,WHSV: 2h^{-1}



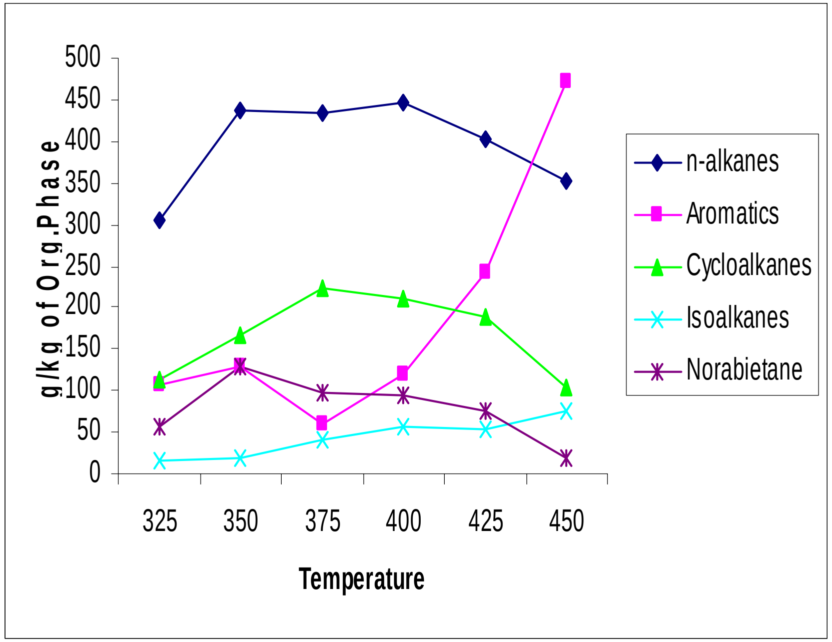
HDO product yields: HDO Vs Decarboxylation
Feedstock: DTO, T = 325-450º C, Pr: 50bars,WHSV: 1.5h^{-1}

More steady state HDO activity at longer residence time

HDO of DTO



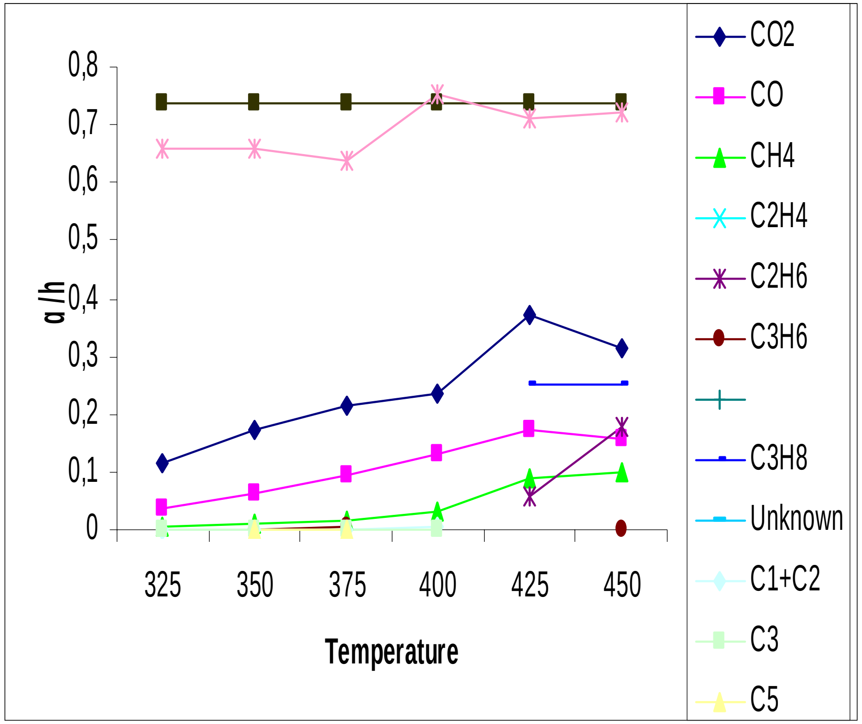
Product distribution:Aromatics Vs Non-aromatics
Feedstock: DTO, T = 325-450º C, Pr: 50bars,WHSV: 2h-1



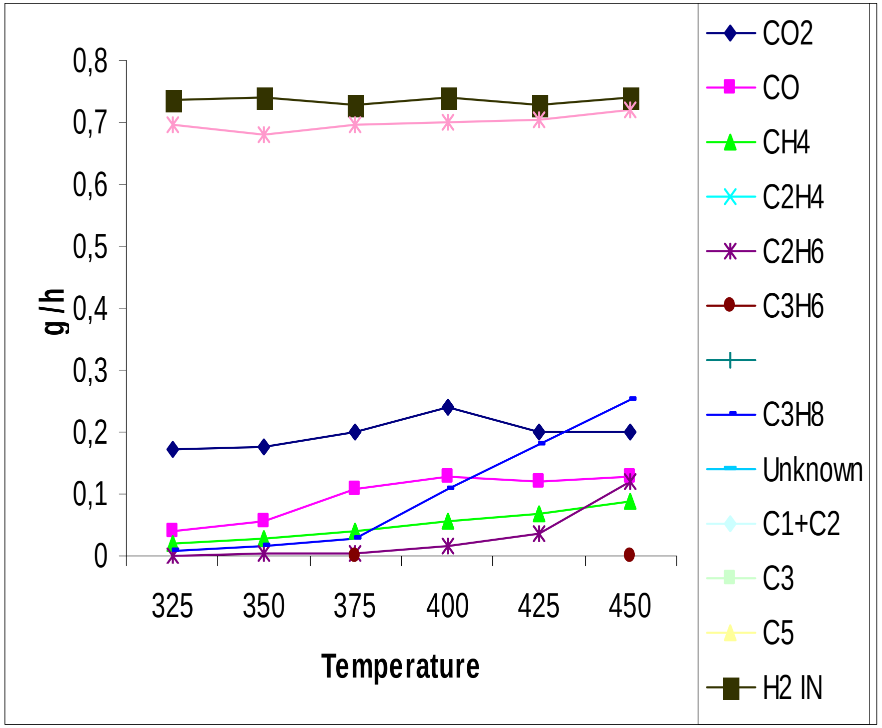
Product distribution:Aromatics Vs Non-aromatics
Feedstock: DTO, T = 325-450º C, Pr: 50bars,WHSV: 1.5h-1

More aromatics at higher temperature espescially at longer residene time

HDO of DTO



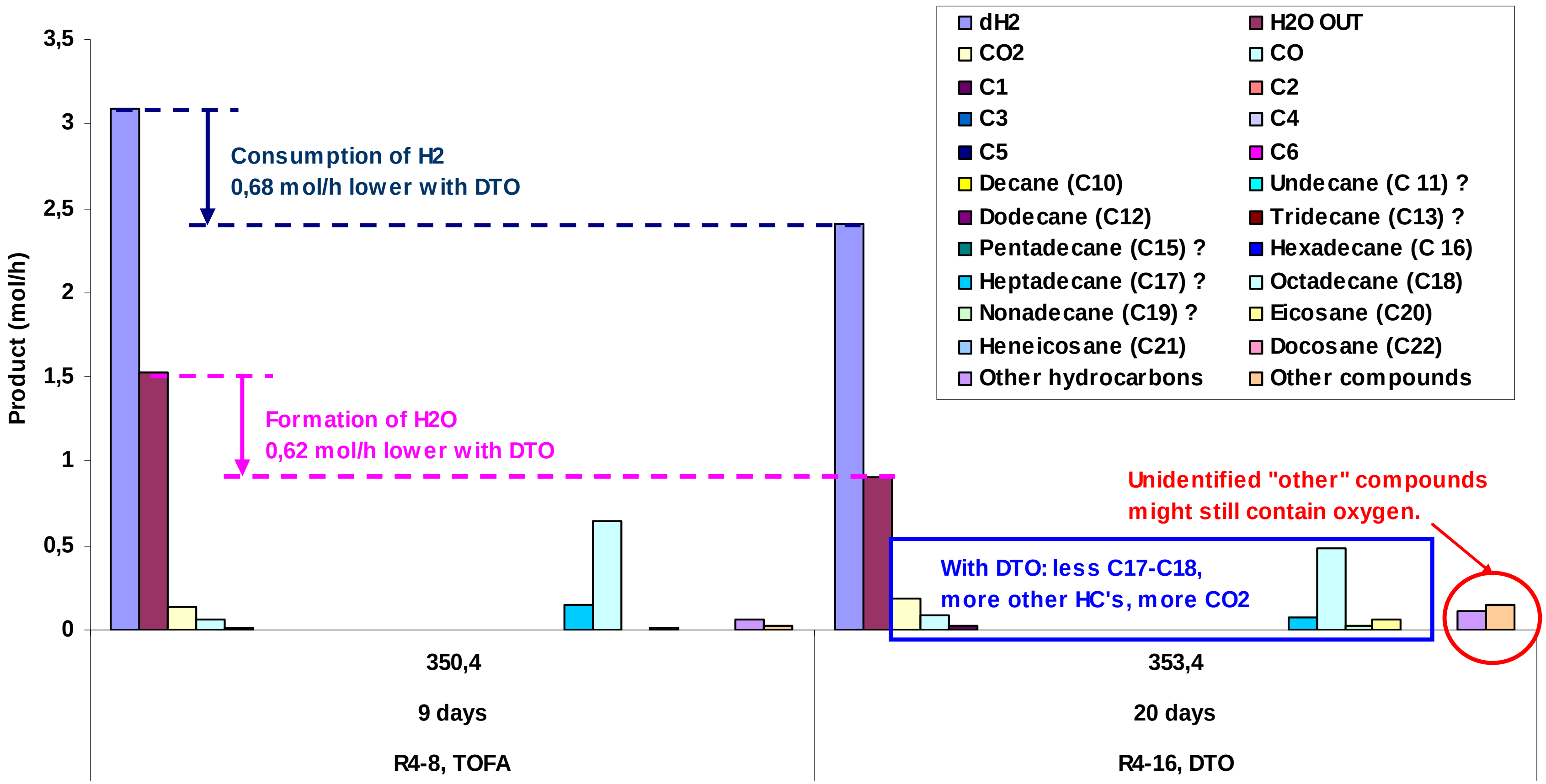
Gaseous products distribution
Feedstock: DTO, T = 325-450º C, Pr: 50bars,WHSV: 2h-1



Gaseous products distribution
Feedstock: DTO, T = 325-450º C, Pr: 50bars,WHSV: 1.5h-1

Reduced decarboxylation rate at longer residence time

HDO piloting studies with TOFA and DTO



Conclusions

- NiMo catalyst shows more HDO activity to TOFA than DTO
- TOFA shows steady state HDO activity with increase of temperature at longer residence time
- With DTO steady state HDO activity can be obtained at longer residence time with increase of temperature
- Catalyst activity of the NiMo catalyst for the HDO of resin acids should be revised
- Piloting Vs Lab scale studies shows similar trend

Acknowledgements

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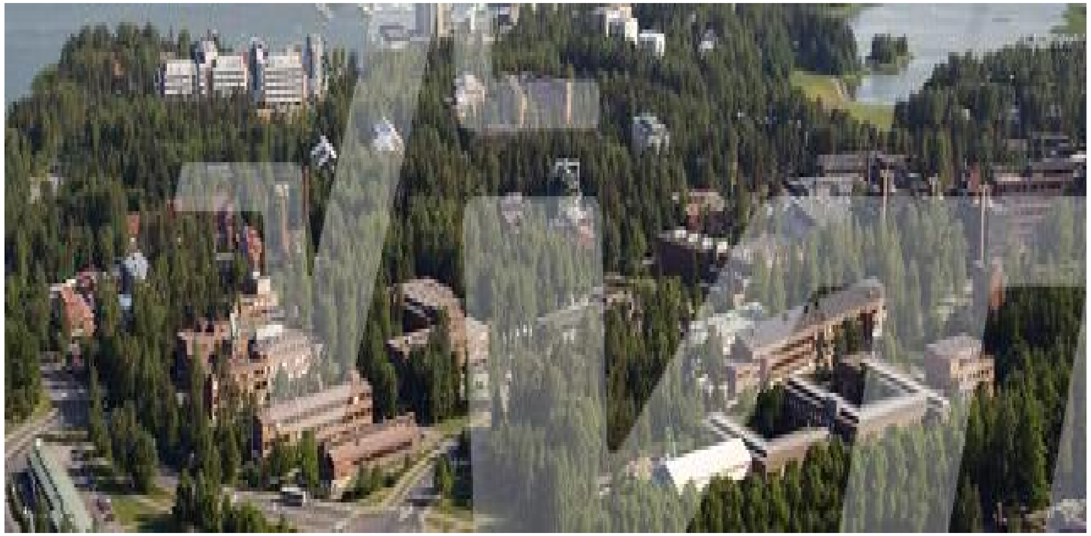
- Dr. Antero Laitinen



THANK YOU FOR YOUR ATTENTION!!

Q&A

VTT creates business from technology