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 materials from woody biomass

Upgrading of Kraft pulping process into a multi-product biorefinery concept
Pulp mill biorefinery

Chips

Bark and forest residue

pulp mill

spent liquor

Cellulose → Biomaterials

Pulp

Up to 50% of Finnish consumption of automotive fuels

Biomass and black liquor gasification

Electric power

Liquid biofuels

Higher hydrocarbons

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

Abietic acid

Dehydroabietic acid

HDO

-\text{H}_2\text{O}

Abietane

Norabietane

Linoleic acid

HDO

Oleic acid

n-Octadecane
Tall Oil Fatty Acid (TOFA) and Distilled Tall Oil composition

TOFA (C\(_{18}H_{32}O_2\)), M = 280.4 g/mol
- C: 76%
- H: 12%
- O: 12%

DTO (C\(_{18}H_{31}O_2\)), M = 279.4 g/mol
- C: 78%
- H: 11%
- O: 11%

Free fatty acids: 96%
Free rosin acids: 1.8%

Free fatty acids: 70%
Free rosin acids: 27%
Mass balance estimation

H2 IN → HDO → H2 OUT
TOFA or DTO IN → HDO → GAS OUT

HC OUT → HDO → HC OUT
Water OUT → HDO → Water OUT

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 = 325-375°C, Pr: 50bars, WHSV: 2h⁻¹

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

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

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

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

Gaseous products distribution
Feedstock: TOFA, $T = 325-375^\circ C$, $P_r: 50$ bars, WHSV: $2h^{-1}$

Gaseous products distribution
Feedstock: TOFA, $T = 325-375^\circ C$, $P_r: 50$ bars, WHSV: $1.5h^{-1}$

Reduced decarboxylation rate at longer residence time
HDO of DTO

HDO product yields: HDO Vs Decarboxylation
Feedstock: DTO, T = 325-450°C, Pr: 50bars, WHSV: 2h⁻¹

More steady state HDO activity at longer residence time

HDO product yields: HDO Vs Decarboxylation
Feedstock: DTO, T = 325-450°C, Pr: 50bars, WHSV: 1.5h⁻¹
HDO of DTO

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

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

More aromatics at higher temperature especially at longer residence time
HDO of DTO

Gaseous products distribution
Feedstock: DTO, $T = 325-450^\circ C$, Pr: 50bars, WHSV: $2h^{-1}$

Gaseous products distribution
Feedstock: DTO, $T = 325-450^\circ C$, Pr: 50bars, WHSV: $1.5h^{-1}$

Reduced decarboxylation rate at longer residence time
HDO piloting studies with TOFA and DTO

Consumption of H₂: 0.68 mol/h lower with DTO

Formation of H₂O: 0.62 mol/h lower with DTO

With DTO: less C₁₇-C₁₈, more other HC’s, more CO₂

Unidentified "other" compounds might still contain oxygen.
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
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Q&A
VTT creates business from technology