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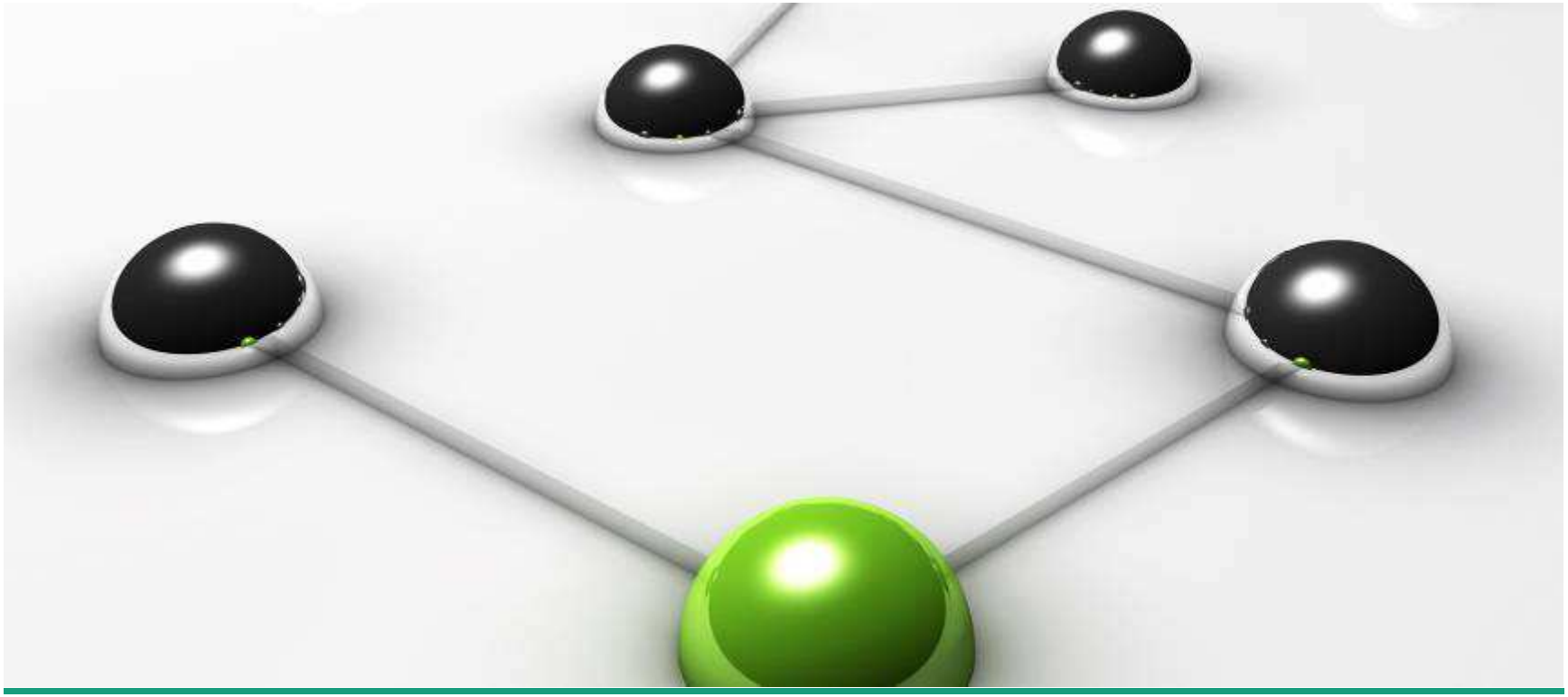
Production of long-chain hydrocarbons from bio-based alcohols

Klaas Breitkreuz, Andreas Menne, **Axel Kraft**

„Biorefineries“, Pucon (CL), 19.11 2012



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AGENDA

- Introduction
  - Fraunhofer UMSICHT, Business Unit: Biofuels
  - Link to PhD research topic
- Basic idea behind the process
- Chain elongation technology
  - Process conditions
  - Chemistry
- Pathway to long chain hydrocarbons
  - Chemistry
- Financial considerations
- Summary

Facts & Data on Fraunhofer UMSICHT

Foundation	1990
Budget 2011	24.8 million € (~40% industry)
Staff	345 (~60% permanent staff)
Spin-Offs	13
Laboratories/Pilot plants	4 500 m²

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Biofuels Unit at UMSICHT – Vision and Scope of R&D

Source: MEV

VISION : Creation of an affordable, sustainable future with chemistry

- Development of catalytic processes for Biofuels & Chemicals
- Screening and (selected) catalyst development
- Scale-up and pilot plant operation
- Employed raw materials are “mainly” bio-based:

  Fats & oils, sugars, alcohols, hemi-cellulose, residues

Member of European Biofuels Technology Platform (workgroup conversion) www.biofueltp.eu

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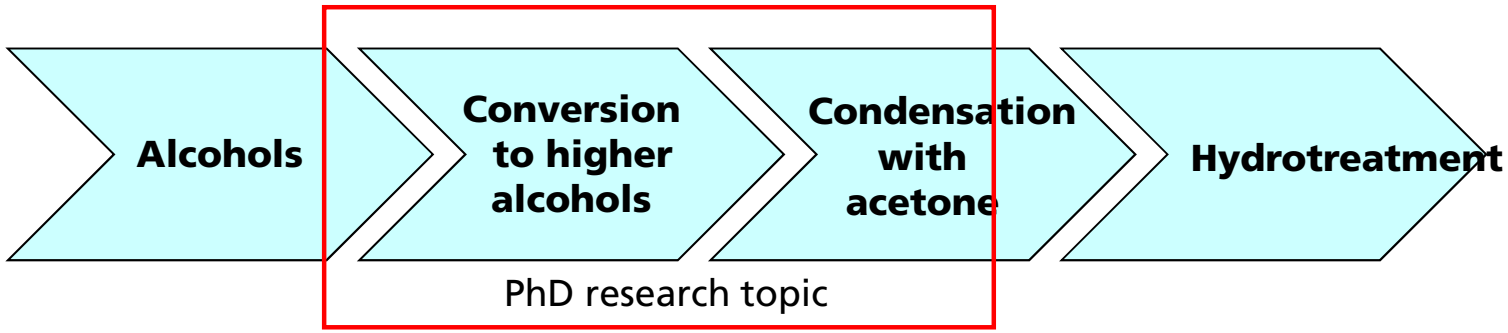
Multistage process to long chain hydrocarbons



- Step 2: Condensation of short-chain alcohols (e.g. ethanol)
- Step 3: Condensation (2:1) of received “higher” alcohols with acetone

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Why ethanol as raw material?

- Current situation
  - Chemical and Fuel Industry want to move away from fossil based raw materials
  - Large quantities of ethanol expected, when 2nd–generation process available, e.g.: fermentation of cellulose, CO-fermentation (Lanzatech, Ineos)
  - This opens up new opportunities to use ethanol as green raw material
- Problem: Ethanol as such has many disadvantages (limited compatibility with fuels and low value as chemical or fuel)

  → Solution: Chain elongation process to higher alcohols based on ethanol

Ethanol based green chemicals and fuels

- UMSICHT R&D: Catalytic condensation of ethanol to higher alcohols (PhD research topic)
- Goal: Green and economically attractive process with fit to refinery or chemical site
- Product application areas of higher alcohols:
  - Biofuels (kerosene, gasoline, diesel booster)
  - Chemicals (solvents, plasticizers, alkenes)
- Patents: **2x Fraunhofer UMSICHT,** 13x DuPont, 1x Sangi

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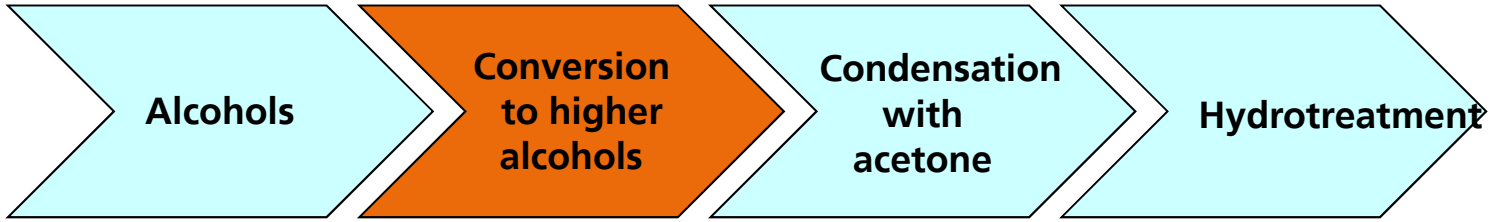
Alcohol condensation process



- Fully automated Mini-Plant
  - 1-100 bars
  - Up to 450 °C
  - Max. 3 l/h feed
  - 24/7-mode
- Optional H_2-dosing
- Closed mass-balance

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Conditions for alcohol condensation

- Process conditions:
  - 1-80 bars absolute
  - 280 – 380 °C
- Raw materials:
  - Alcohols
  - Aldehydes
- Conversion rate: up to 90 %

- Catalyst:
  - Carbon based
  - Commercially available
  - Long-term stable under reaction conditions
  - Tolerates water

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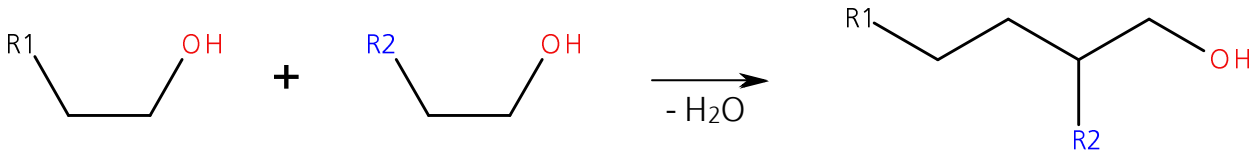
Chemistry

- Gas-phase condensation of alcohols



- Products: linear and branched alcohols plus water
- Co-products: corresponding aldehydes, H_2
- Degree of consecutive reactions depends on residence time (conversion), temperature and pressure
- Tailor-made distribution and branching

R1, R2 = H, CH_3, $CH_3(CH_2)_n$

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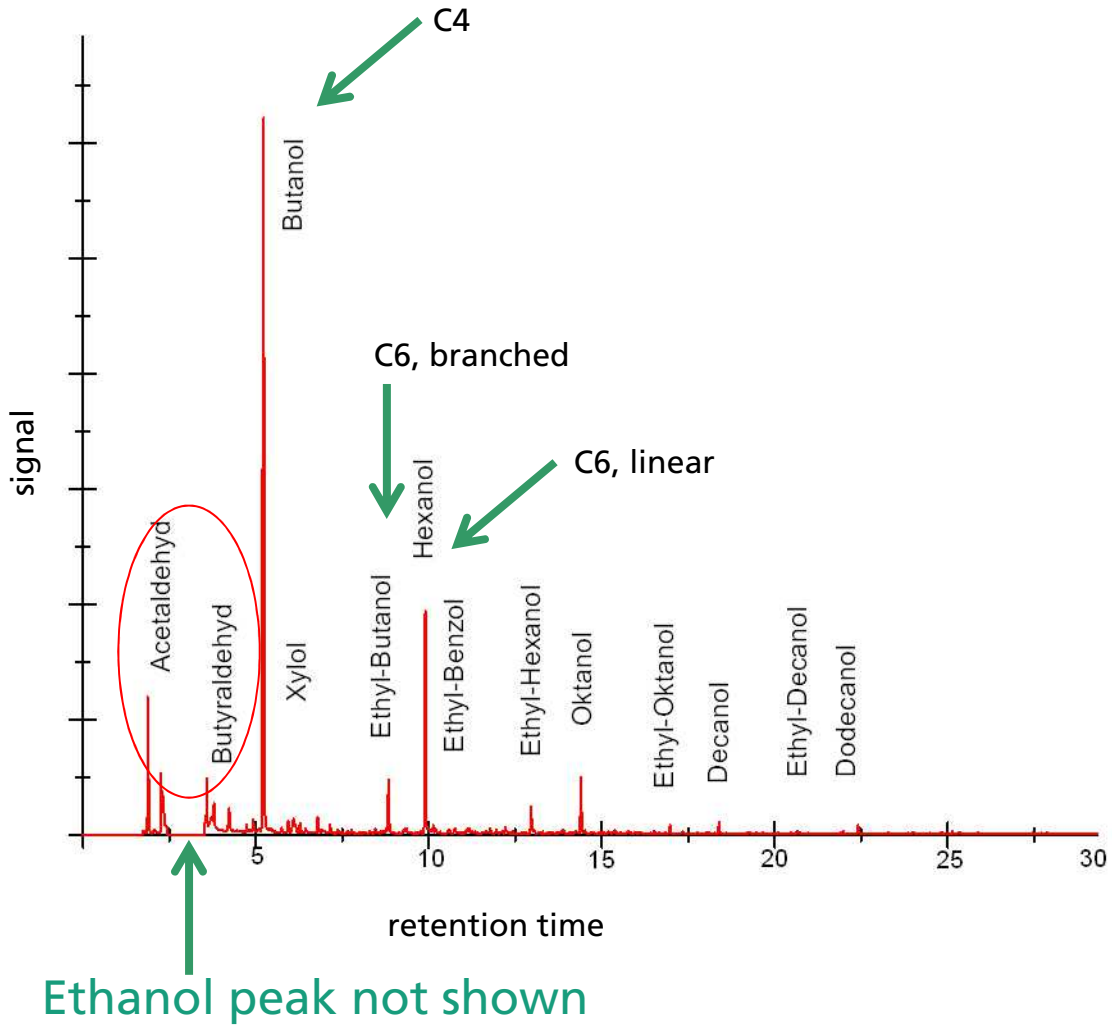
Results: Condensation of ethanol to butanol, hexanol

Example GC/FID of typical product mixture

- Pure ethanol as feed
- Gas-phase reaction
- Conversion EtOH: 26%
- > 97% identified
- Min. gaseous products
- Also water in product
- Low pressure



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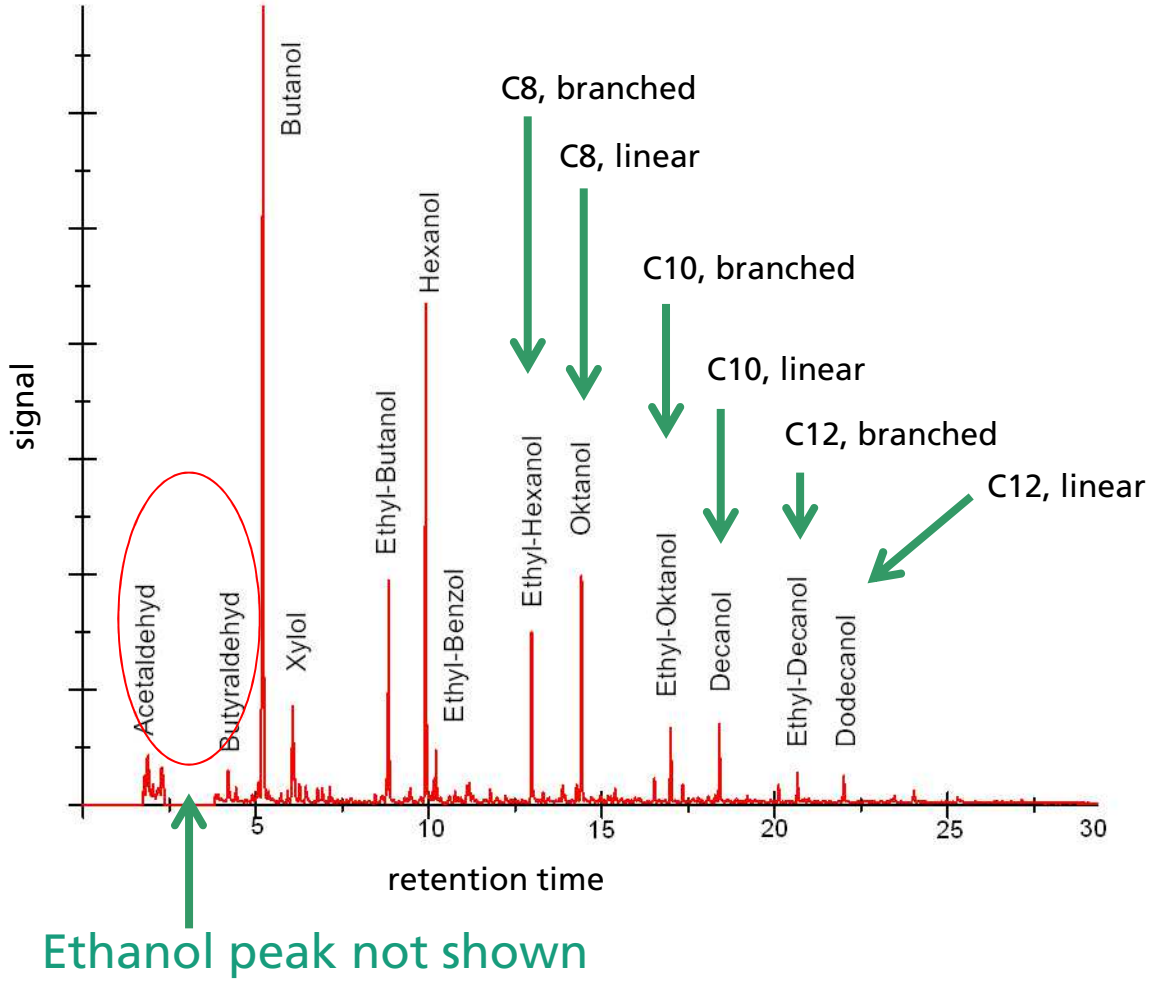
Results: Condensation of ethanol to higher alcohols

Example GC/FID of typical product mixture

- Pure ethanol as feed
- Gas-phase reaction
- Conversion EtOH: 53%
- > 94% identified
- Min. gaseous products
- Also water in product
- Medium pressure



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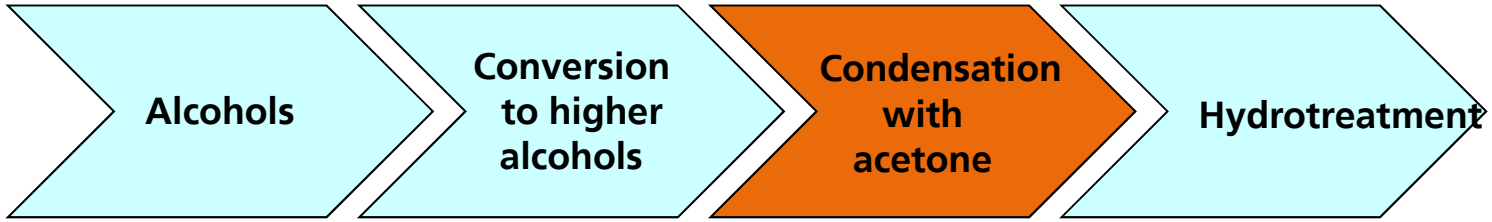
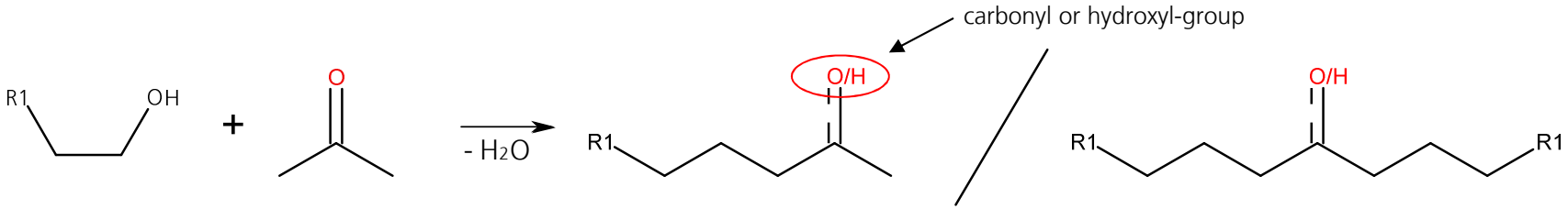
Multistage process to long chain hydrocarbons



- Step 3: Condensation (2:1) of received “higher” alcohols with acetone

Pathway to long chain hydrocarbons

- Condensation of intermediate higher alcohols with acetone:

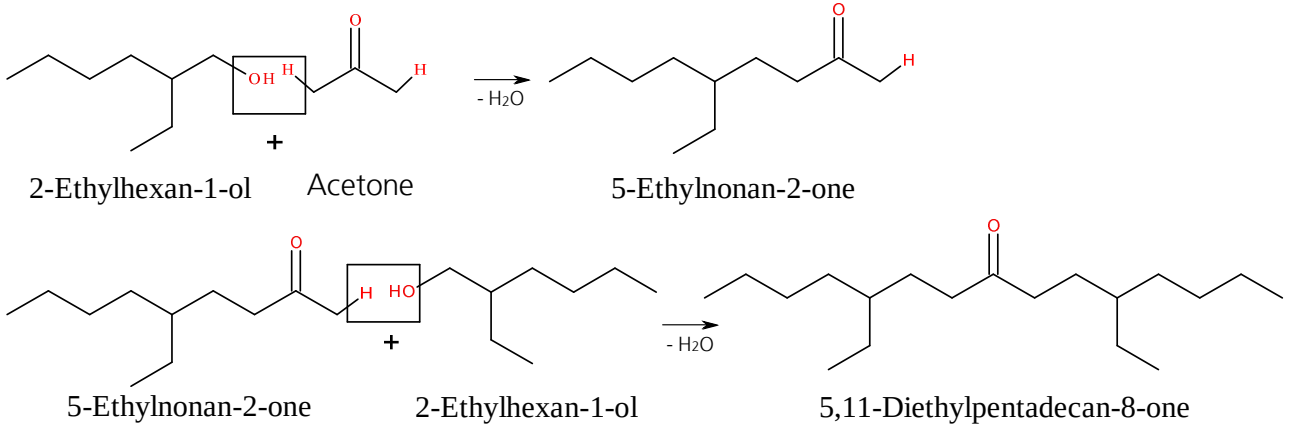


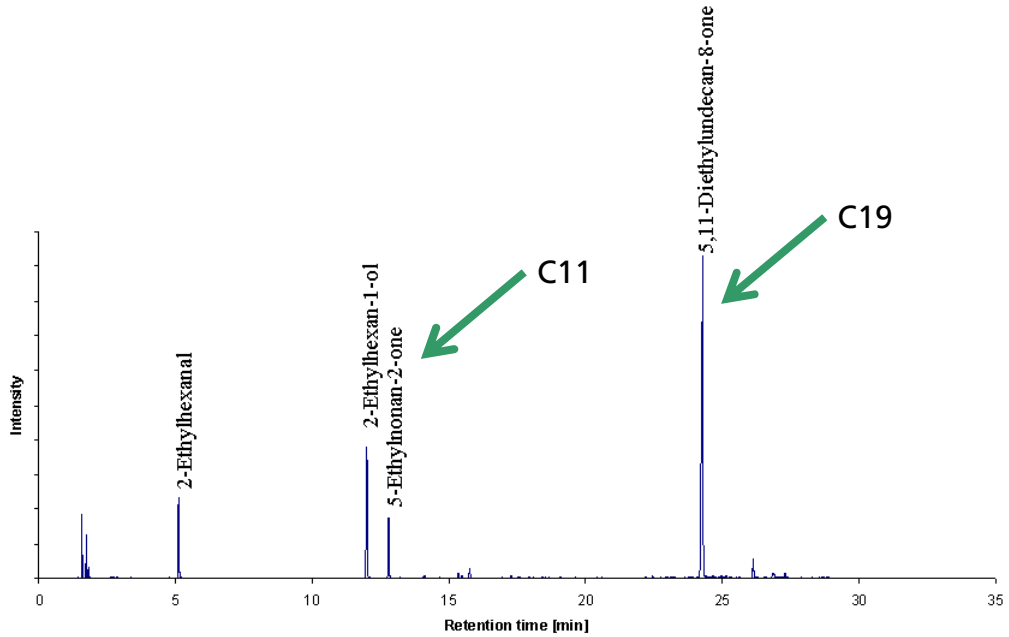
R1 = H, CH_3, $CH_3(CH_2)_n$, linear and branched

- Condensation possible with linear and/or branched alcohols
- Products: linear and branched ketones and sec. alcohols with tailor-made distribution
- Similar conditions as alcohol-condensation-step, but different catalytic pathway
- **Only 1 oxygen** atom per target molecule left → removal by hydrotreating* to yield kerosene and/or diesel fractions

*Corma, Angew. Chem. Int. Ed. 2011, 50, 2375 –2378
DOI: 10.1002/anie.201007508

Condensation of Ethylhexanol and Aceton (1:2)





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Condensation of alcohols/acetone ex ABE-process

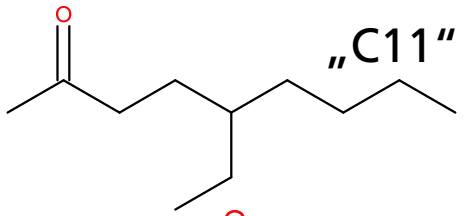
„All-in-one-condensation" of acetone, butanol, ethanol

Conversion to higher alcohols

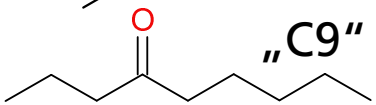
- ethanol + butanol = hexanol
- hexanol + ethanol = 2-ethylhexanol (2-EH)

Condensation with acetone

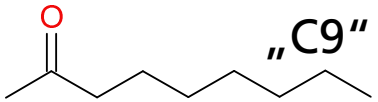
- acetone + 2-EH =



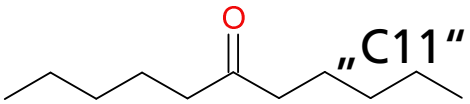
- acetone + butanol + ethanol =



- acetone + hexanol =



- acetone + 2 butanol =



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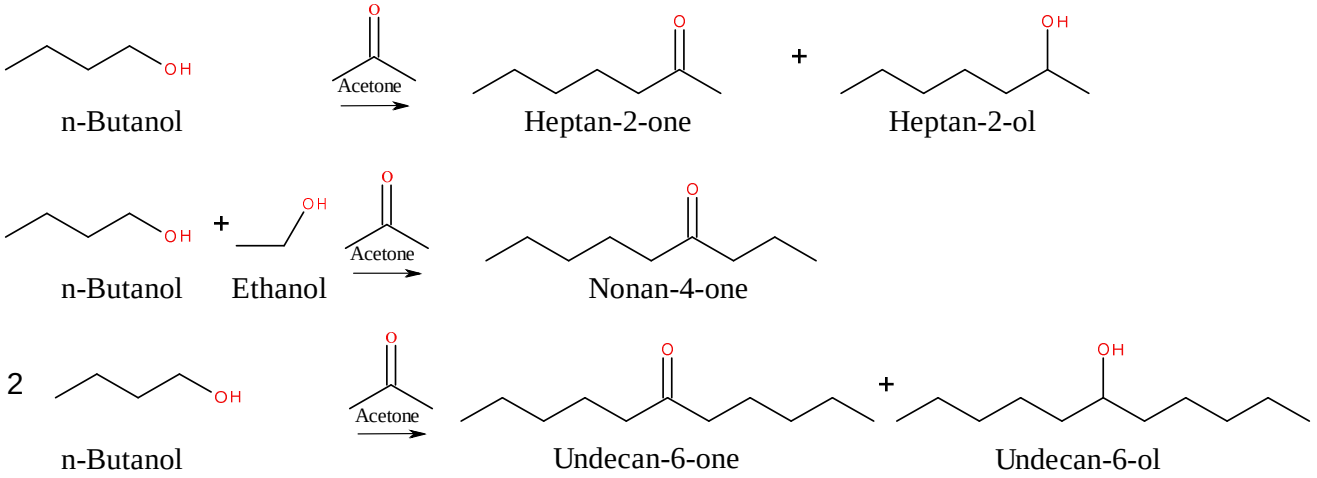
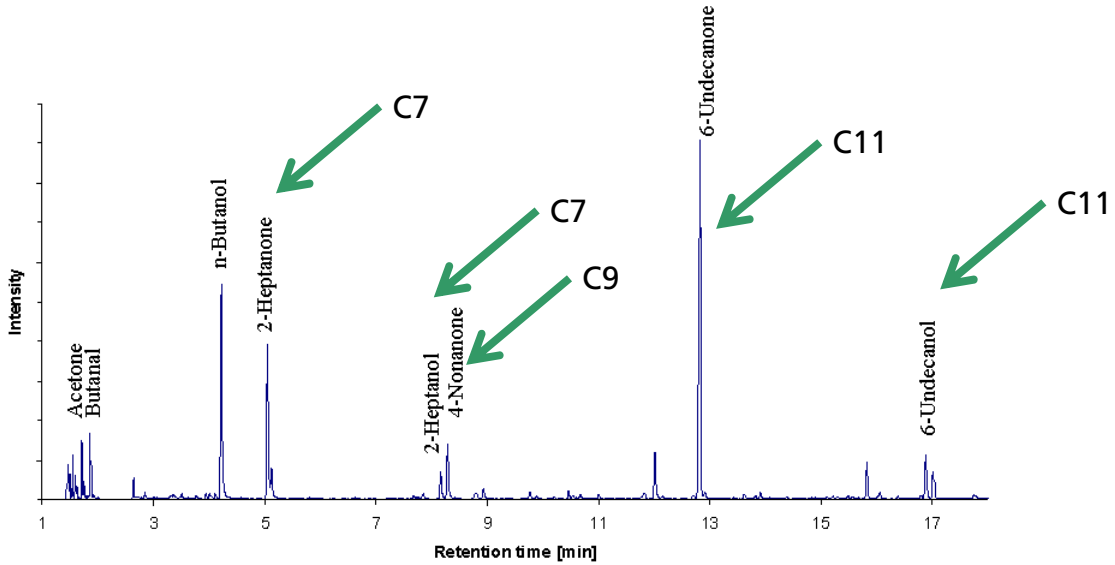
Condensation of aqueous ABE-fermentation broth





acetone:butanol:ethanol = 3:6:1 molar + 10wt% H_2O

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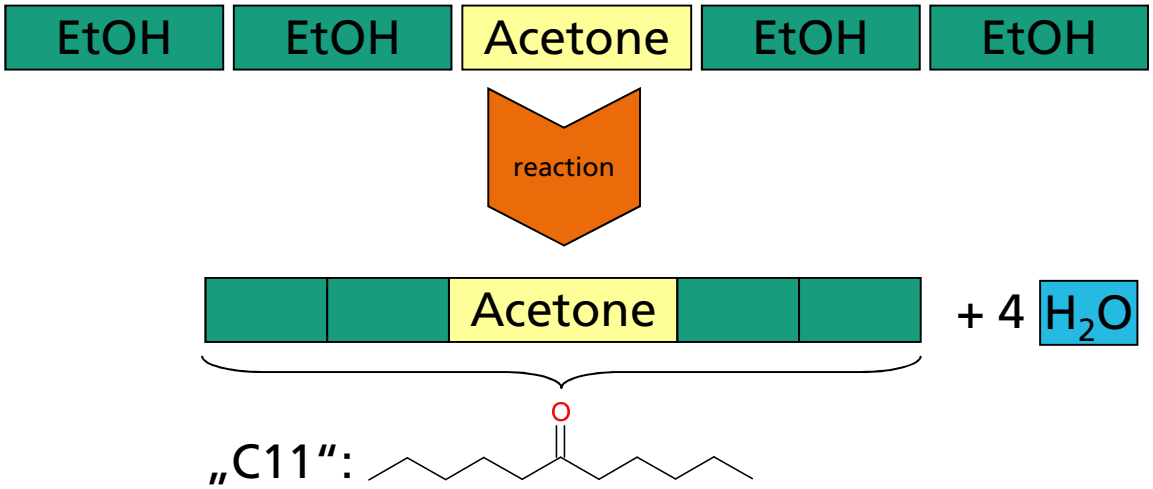
Financial considerations

Best-case-scenario: minimum product price based on raw materials illustrated by target molecule: C11



t/t product	Price US$/t Input	US$/t product
1.08	450 US$/t*	487
0.34	800 US$/t **	273
	Total	**760**

	g/mol
Acetone	58
EtOH	46
C11	170

*LanzaTech, 6/2011, CO-steel mill
** icis.com, 12/2011, fossil based

Summary and Outlook

- A new process chain producing mainly kerosene typical hydrocarbons based on non-food raw materials (ethanol, acetone) has been presented
- Based on stable and commercially available catalysts the process chain is ready for scale-up (larger scale demonstration of step 2 and 3 is required)
- Hence, large amounts of affordable bio-kerosene can be produced soon without taking high R&D-risks
- Fermentation of carbon monoxide to acetone (e.g. Lanzatech) would provide an additional green technology boost when becoming commercial (currently about 73% of “C11” is “green”)
- Lower-cost-route compared to kerosene from FT or HVO
- Fraunhofer is open for cooperation and joint technology development

Source: MEV

Thank you for listening

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