Biorefinery: petrochemicals processing of renewable feedstock

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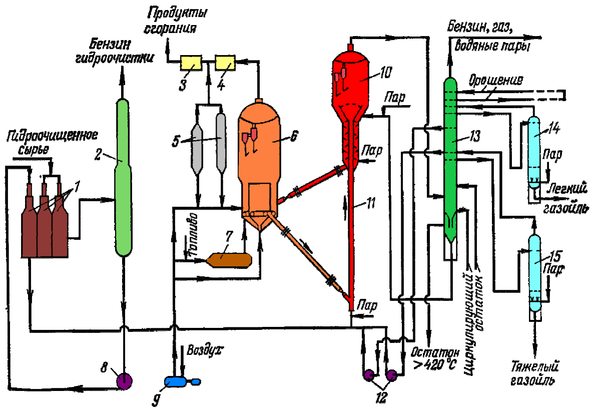
TIPS RAS: Petrochemistry & Oil Refinery

More than 75 years expertise in Petrochemistry and Oil refinery:

- Fluid Catalytic cracking
  9 industrial units in the world
- Visbreaking of heavy residue
  4 industrial units in the world
- Catalytic dewaxing
  2 industrial units in Russia
- Acid-catalyzed homogeneous alkylation processes
  15 industrial units in the world
- Alkylation process based on zeolite catalysts
  1 industrial unit



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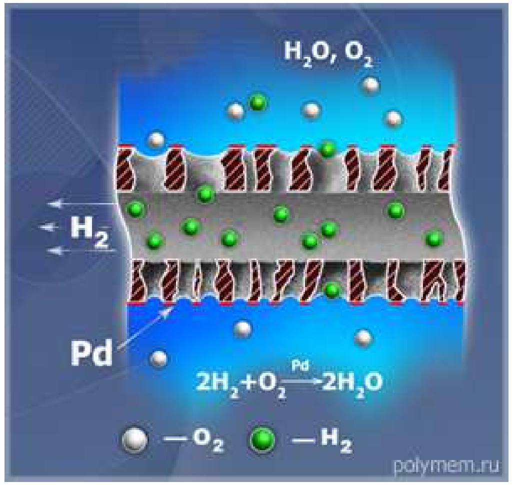
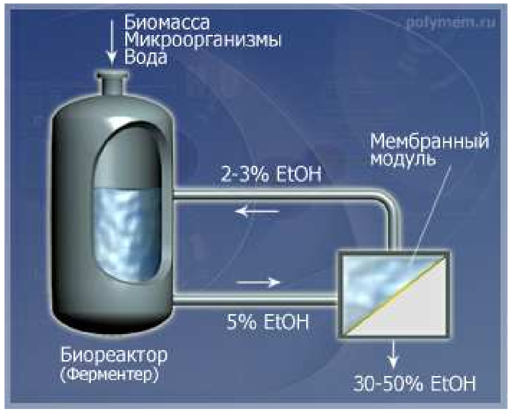
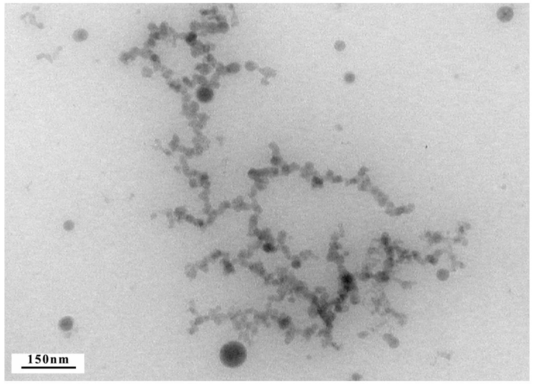
TIPS RAS: Membrane science and technology





- More than *35 years* of expertise in membrane science and membrane technology.
- New area, *membrane catalysis*, was created by Prof. M.V.Gryaznov in TIPS RAS.
- Deep expertise in development of novel membrane materials (e.g. high permeable glassy polymer) *1970th*: first industrial gas separation membranes based on PVTMS.

TIPS RAS: Polymers and Nanocomposites



- More than 45 years of expertise in polymer science (novel polymers for different applications).
- Significant contribution in theory of macromolecular reactions and polymer modification.
- Polymer processing: rheology and introduction of nanocomposites.
- Biomedical polymers and drug delivery systems.
- Composite materials.
- Product commercialization (e.g. adhesives for biomedical applications).

Overall strategy

1. Integration with existing processes

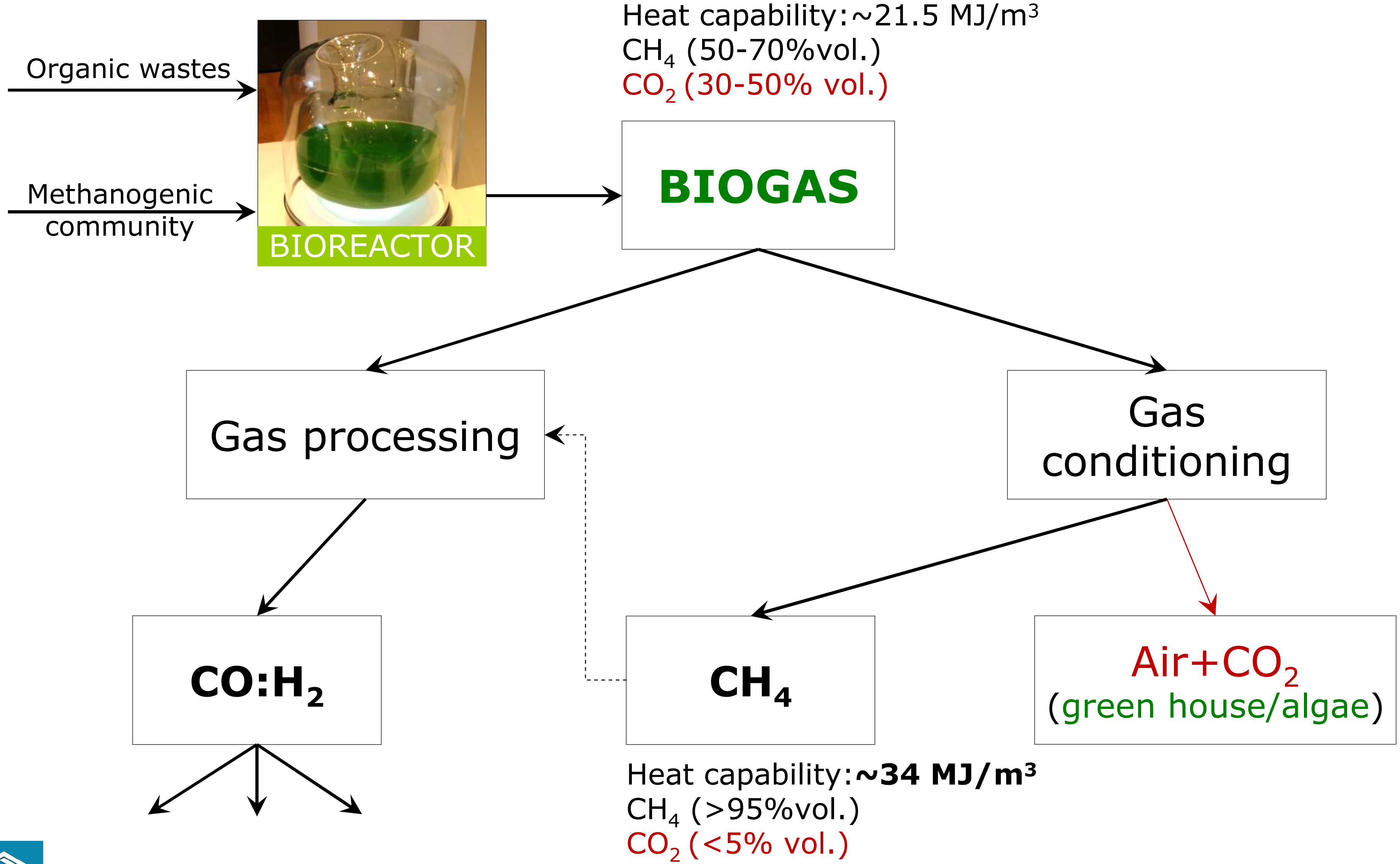
- Same process principles used refinery and chemical plants.
- Introduction and further increasing of renewable feedstock part.

2. Flexibility in process scheme

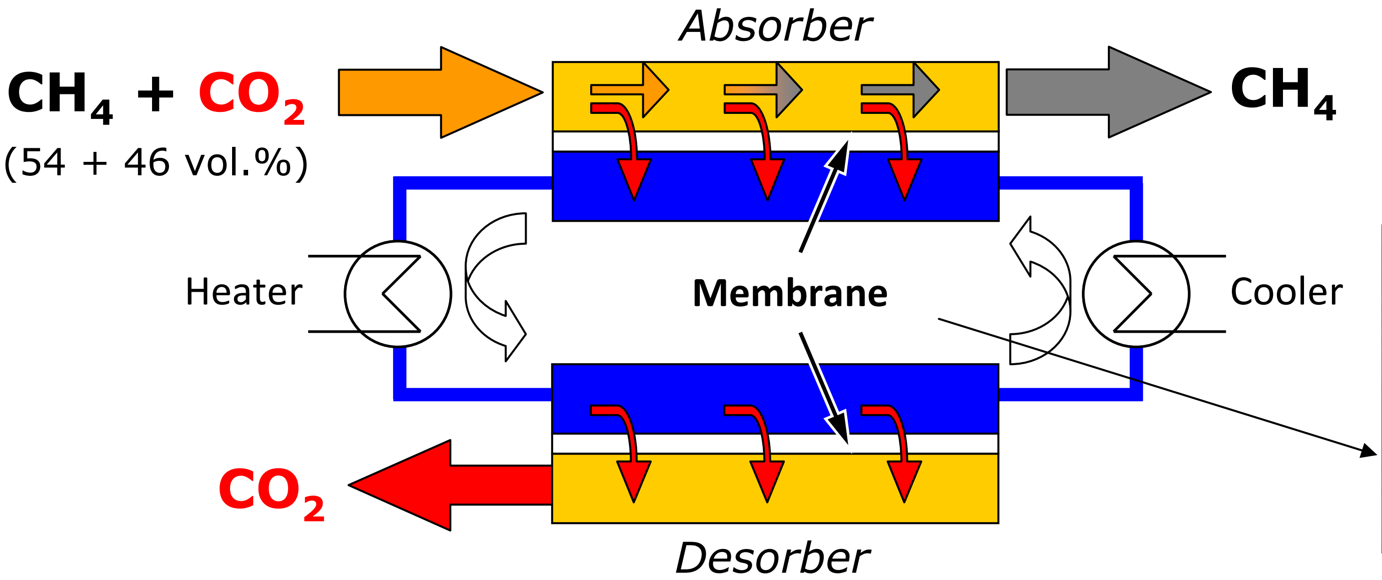
- Utilization of “waste” by-products into new valuable products.
- Variability of products composition by control of catalyst and process conditions.

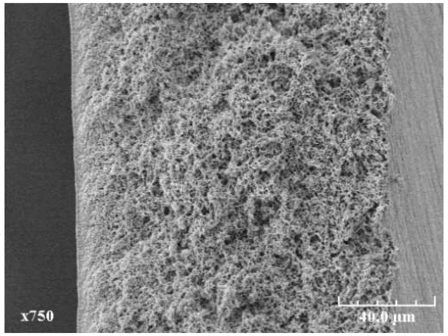
Organics to gas

Biogas: flexibility in processing



Biogas conditioning: membrane contactors for CO_2 capture

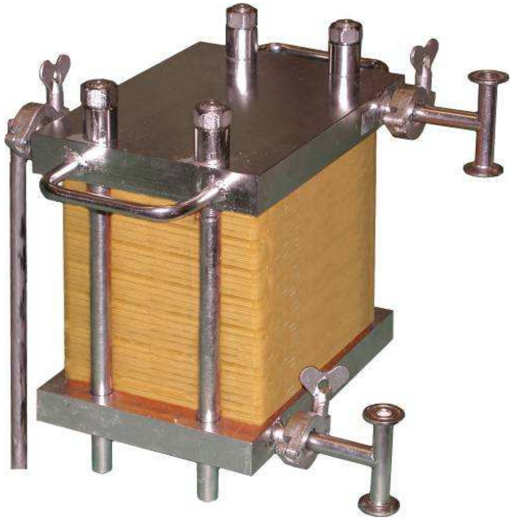




Solvent	T_{des}, °C	Gas composition (%)			
		Absorber		*Desorber*	
		CO_2	CH_4	CO_2	CH_4
H_2O	18	16	84	73	27
K_2CO_3	18	26	74	92	8
K_2CO_3	60	5	**95**	**99.6**	0.4

Biogas conditioning: pilot testing

Membrane module



Upscale

Unit capacity: 50 m^3 biogas/hour

Membrane module parameters:

Size, mm:	250x180x250
Membrane area:	5 m^2
Packing density:	450 m^2/m^3

Biogas processing to syngas

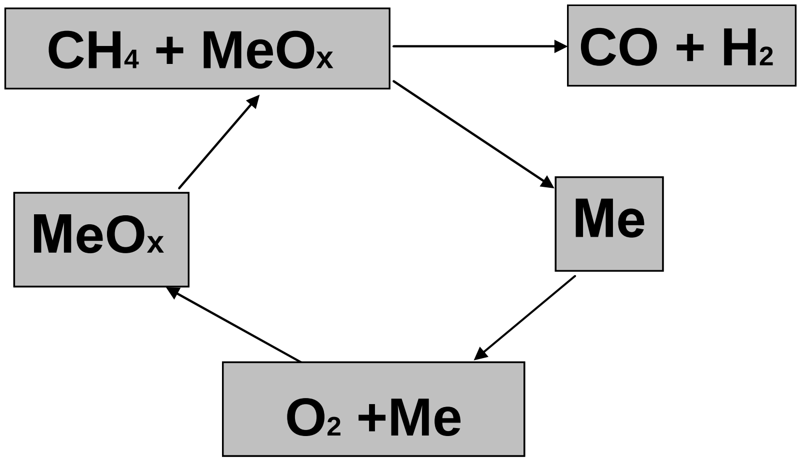
Major drawbacks in biogas processing to syngas:

- **Steam reforming:** CO_2 content in biogas should be lower than 20% to avoid coke formation.
- **Oxidation process:** Oxygen production unit significantly increase CAPEX. If oxygen is replaced by air, additional separation unit is required to remove ballast gases (mainly, nitrogen) from syngas.

Solution:

- **Partial oxidation in chemical reactor:** no limitations for CO_2 content in biogas!
- **Membrane catalytic systems:** compact device.

Biogas processing to syngas



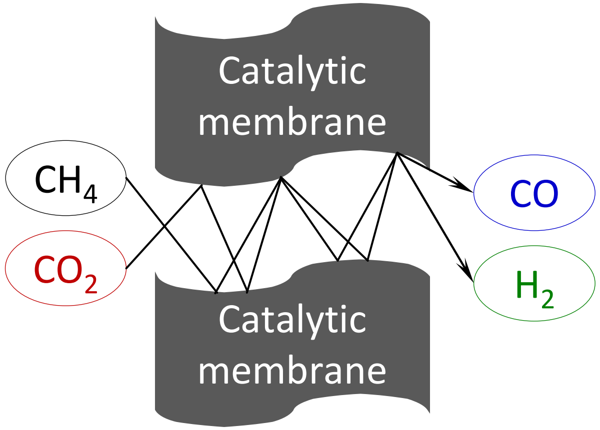
$$CH_4 + [O] \rightarrow CO + 2H_2 \qquad (1)$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (2)$$
$$H_2 + [O] \rightarrow H_2O \qquad (3)$$
$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (4)$$

Pilot unit

Advantages:

- In this approach, there is no nitrogen in syngas.
- Low explosion risk.
- Possibility to varying of syngas composition.

Biogas processing to syngas in membrane reactor



$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

$CH_4 + [O]_s \rightarrow CO + 2H_2$ (1)

$CH_4 + 4[O]_s \rightarrow CO_2 + 2H_2O$ (2)

$CH_4 \rightarrow C + 2H_2$ (3)

$C + CO_2 \rightarrow 2CO$ (4)

$CO + H_2O \rightleftarrows CO_2 + H_2$ (5)

$[O]_s$ – "structured" oxygen

Advantages:

- Decreasing of unit size and catalyst consumption.
- Decreasing of side reaction due to lower contact time in reaction zone.

Support	Active components (oxides)	Productivity, $L/h \cdot dm^3_{membr}$	Syngas composition, H_2/CO	Conversion, %vol.	
				CH_4	CO_2
Ni-Al (granules)	La-Ce	250	0.66	10.3	6.8
Ni-Al (**membrane**)	La-Ce	**3780**	0.63	**51.2**	**26.1**

$T=600^oC$, $W_{feed}=40$ L/h, $CH_4/CO_2=1$

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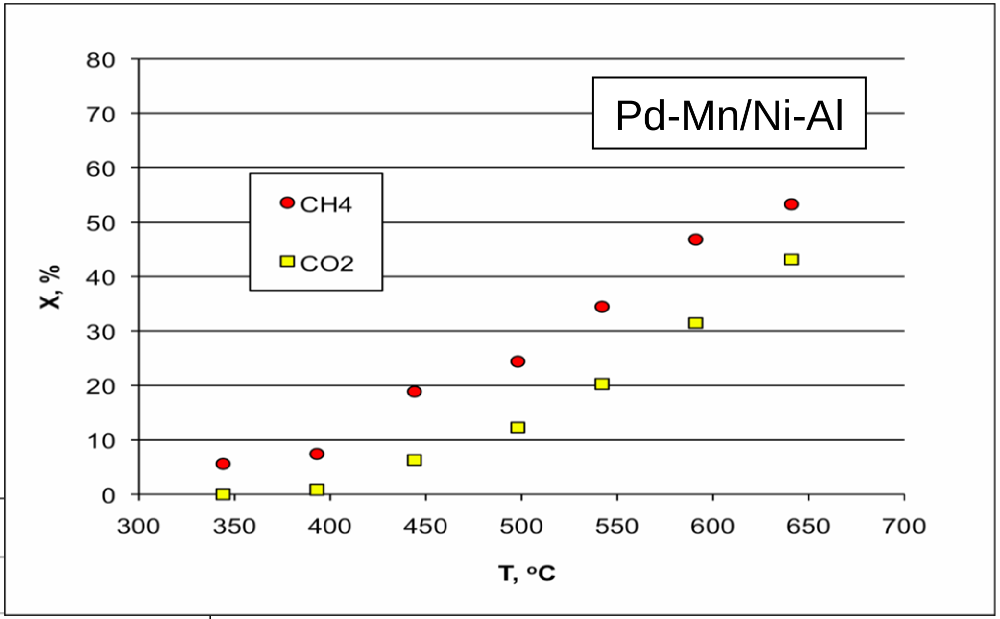
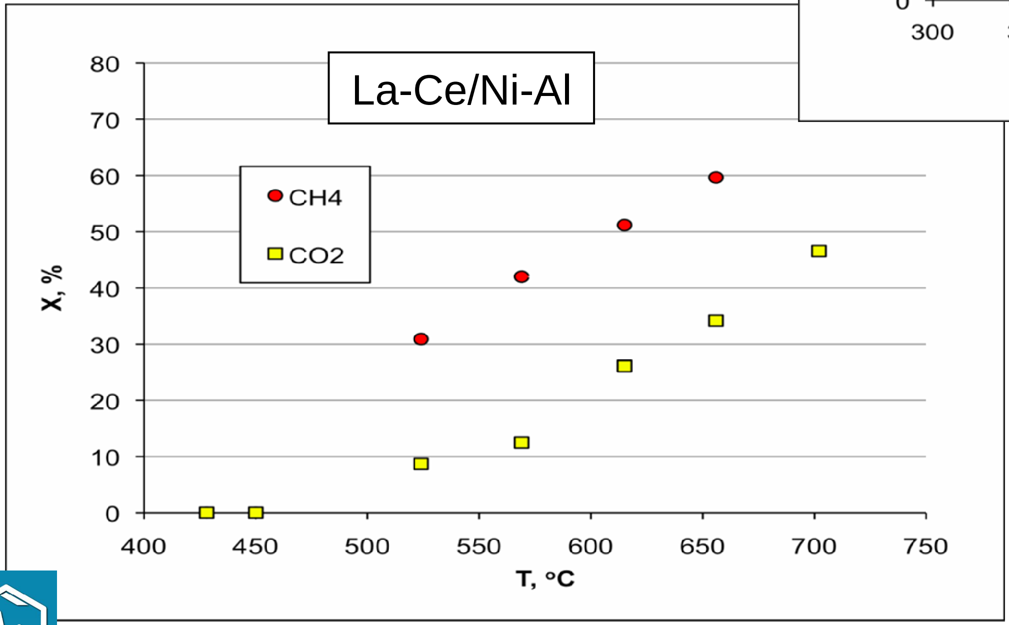
Biogas processing to syngas in membrane reactor

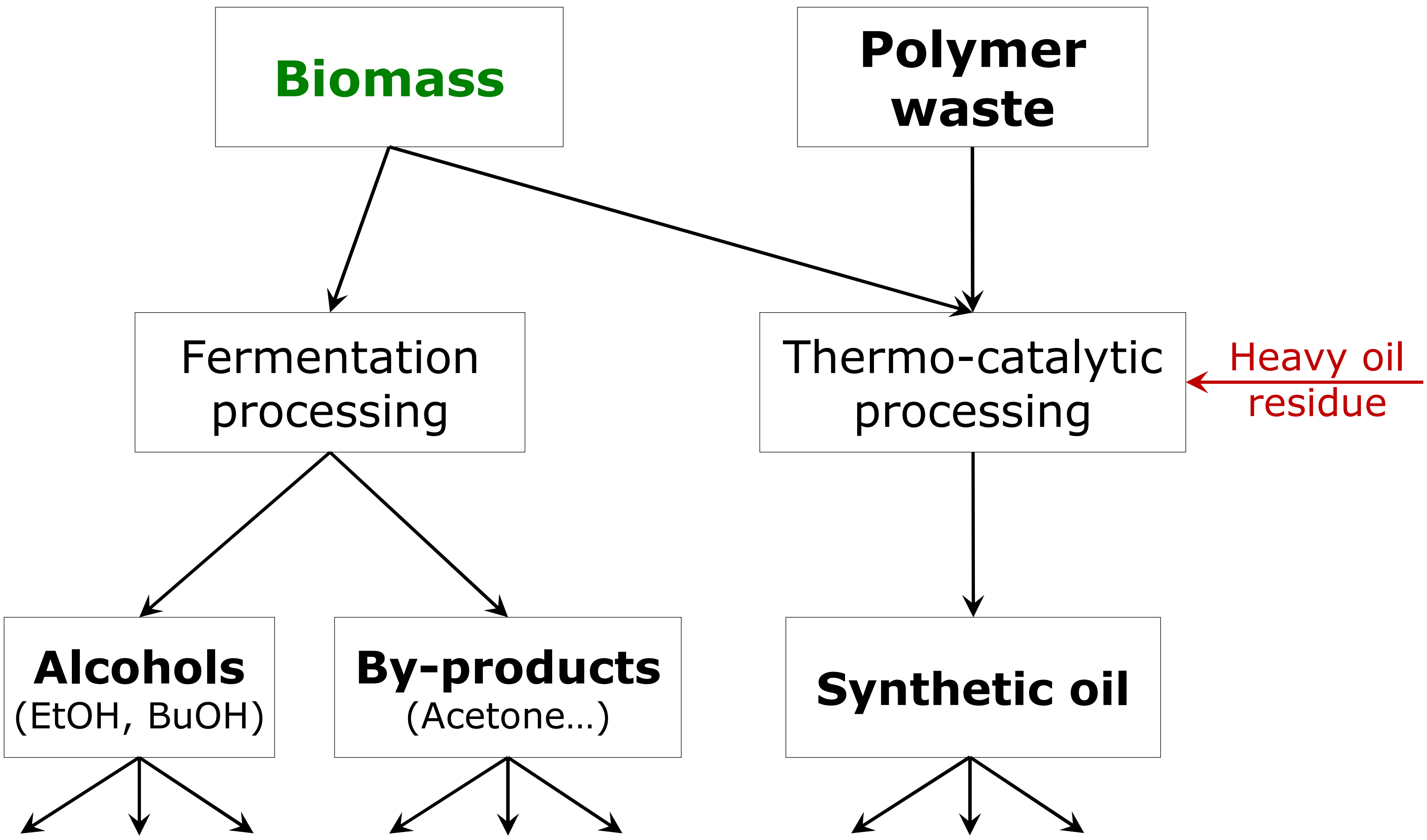
Optimized membrane/catalytic system: conversion of CH_4 and CO_2 as a function of T





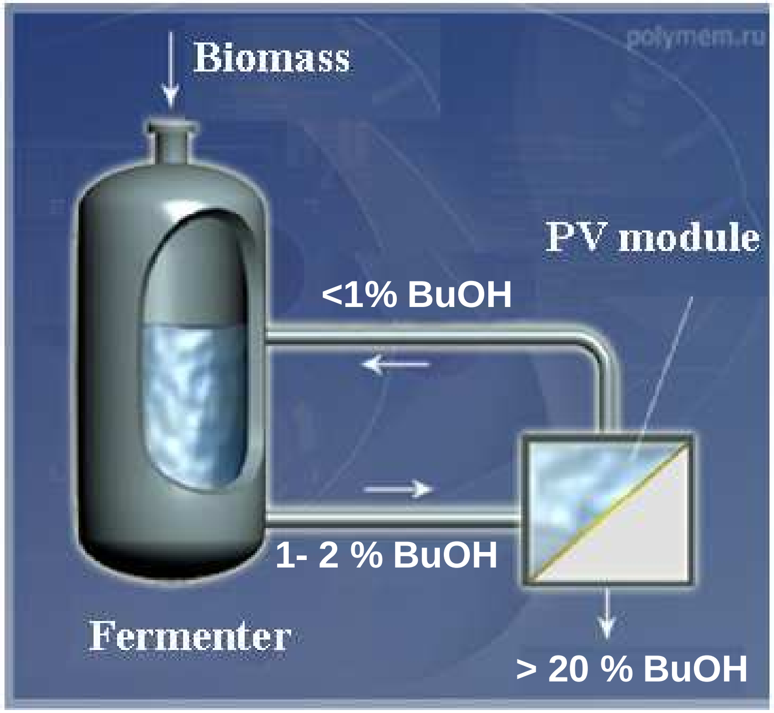
Organics to liquid

Biomass and polymer waste: flexibility in processing

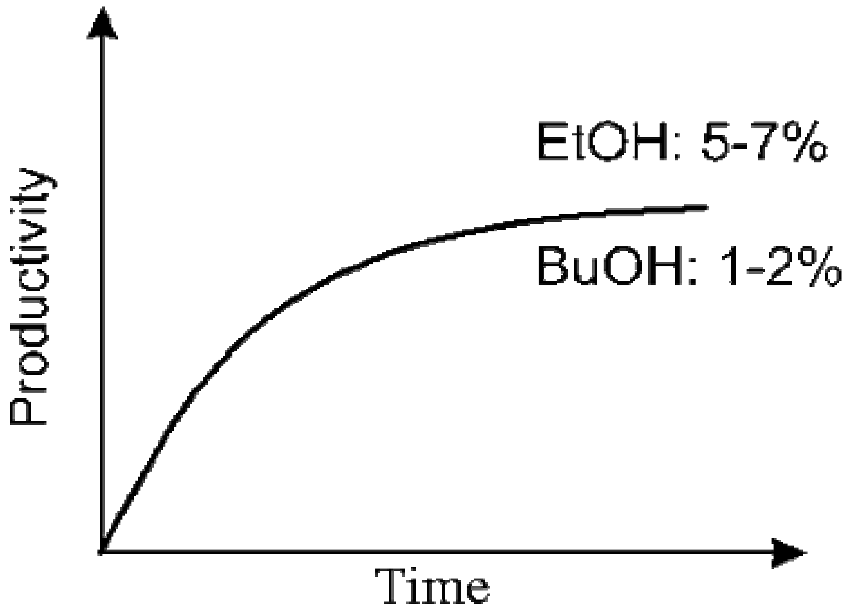


Pervaporation membrane bioreactor: biomass conversion into alcohols

General idea

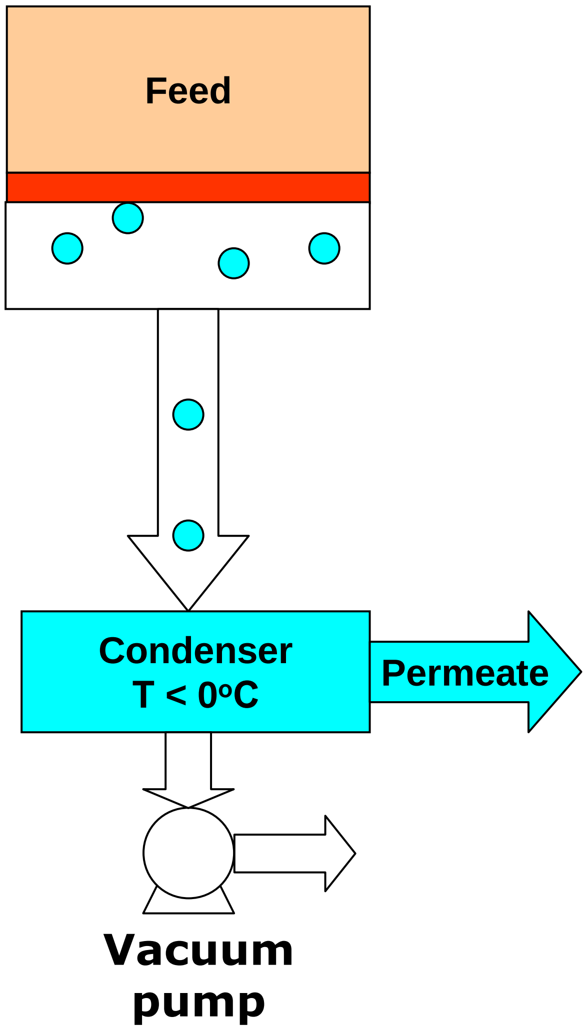


Fermentation product inhibition

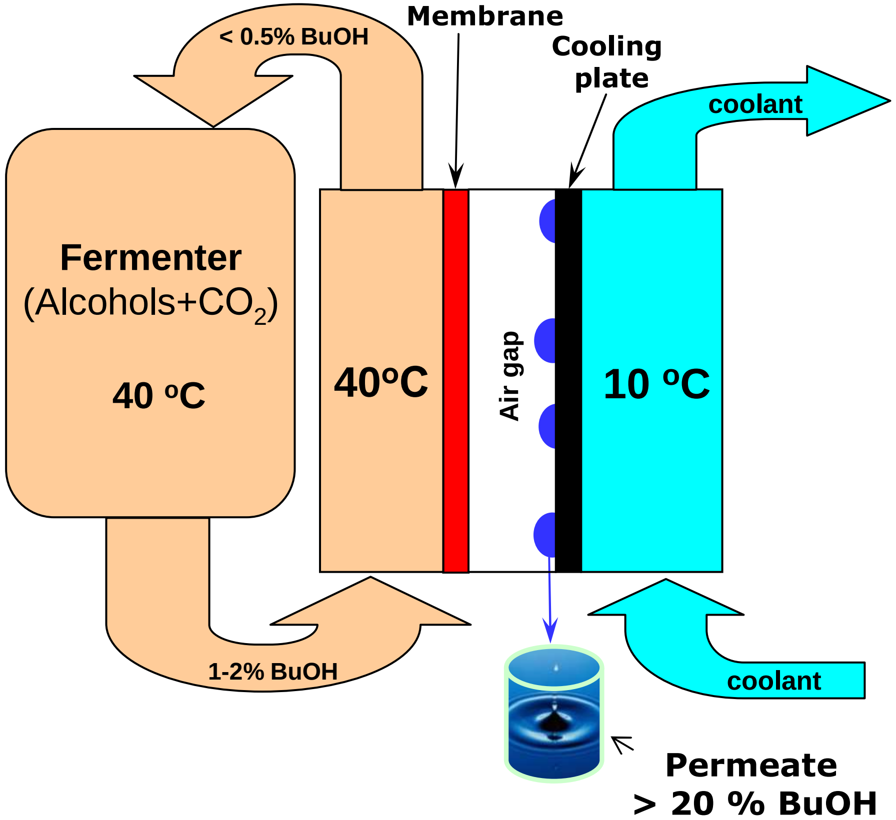


Recovering of organics from fermentation broth: thermopervaporation as a next step in energy efficient PV

Vacuum pervaporation
(conventional approach)



Thermopervaporation



Advantages:

- No vacuum.
- Low condensation temperature 10-20ºC.

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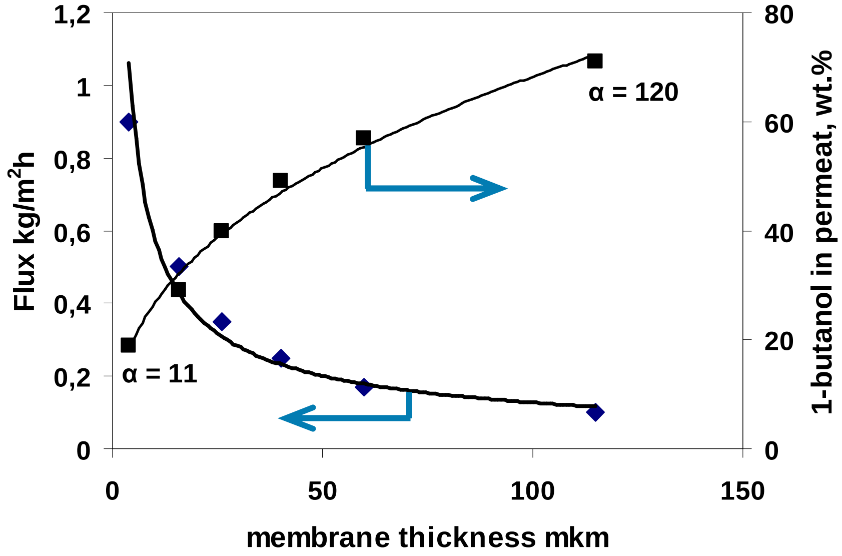
Thermopervaporation: model fermentation mixture

Feed: C_{BuOH}=2 wt.%
ΔT = 45 °C



Model fermentation mixture
Feed temperature: 60°C
Condensation temperature: 15°C

Liquid mixture	wt. %				
	Ethanol	Butanol	Acetone	Butyric acid	Acetic acid
Feed	0.15	1.00	0.45	0.10	0.40
Permeate	0.74	20.41	1.70	0.07	0.15

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Alcohol conversion

Catalyst	Hydrocarbons	Fraction of non-linear molecules, %
Pt/Al_2O_3	Alkanes	6-8
Cu/support	Olefines	25
W-Re	Olefines	50
Pd - Zn	Alaknes+Olefines	50
Pt/Al_2O_3 + MgO + [TiFeZrMo]	Alkanes	91

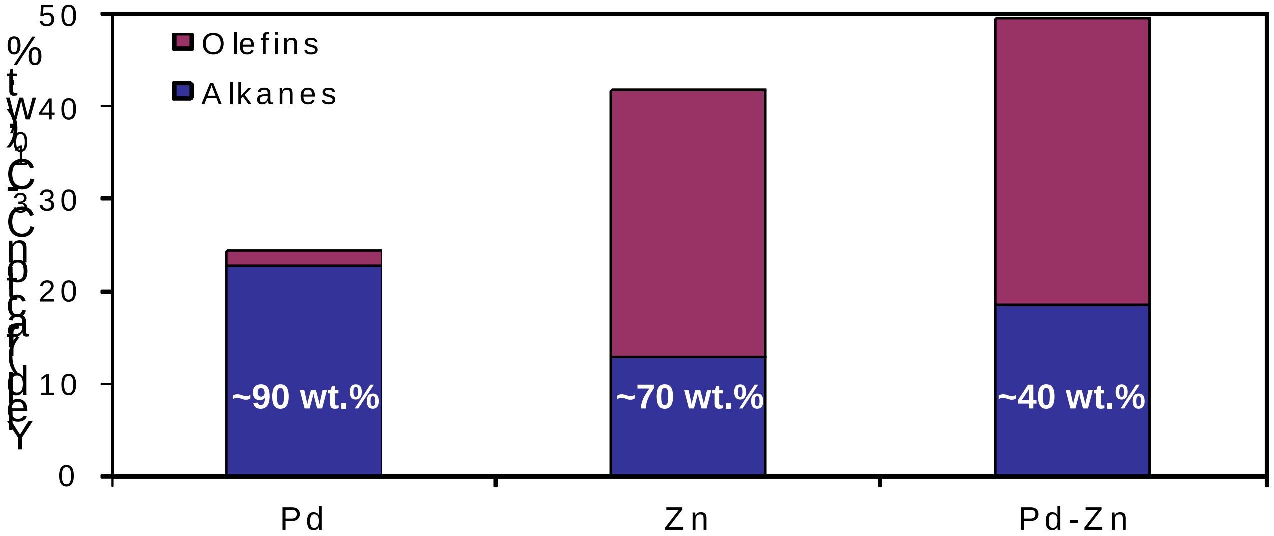
Data for ethanol

Control of product composition:

- Reaction mechanism depends on catalytic system.
- Presence of some compounds could improve total yield and change product composition (*20% glycerin in EtOH → double yield of hydrocarbons*).

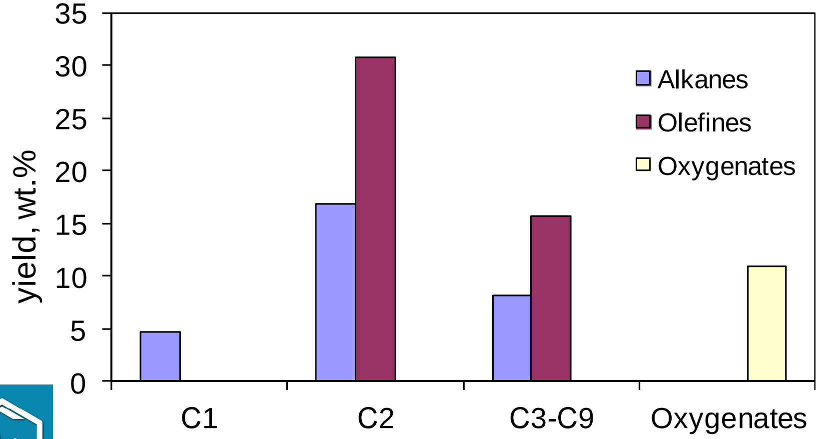
Ethanol conversion: control of process selectivity

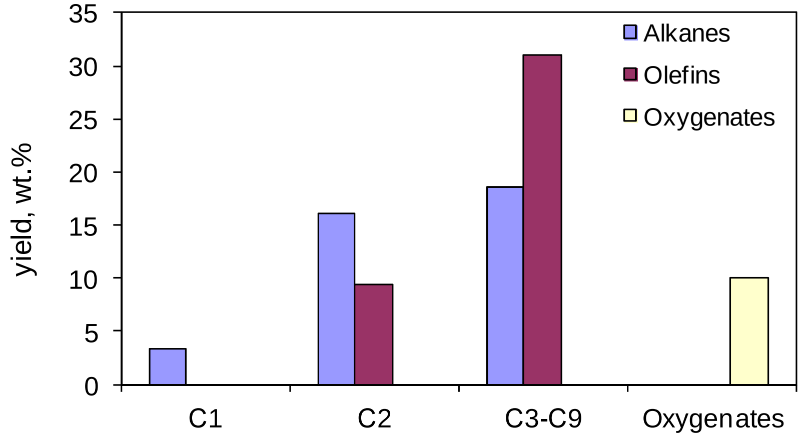
Effect of catalyst type



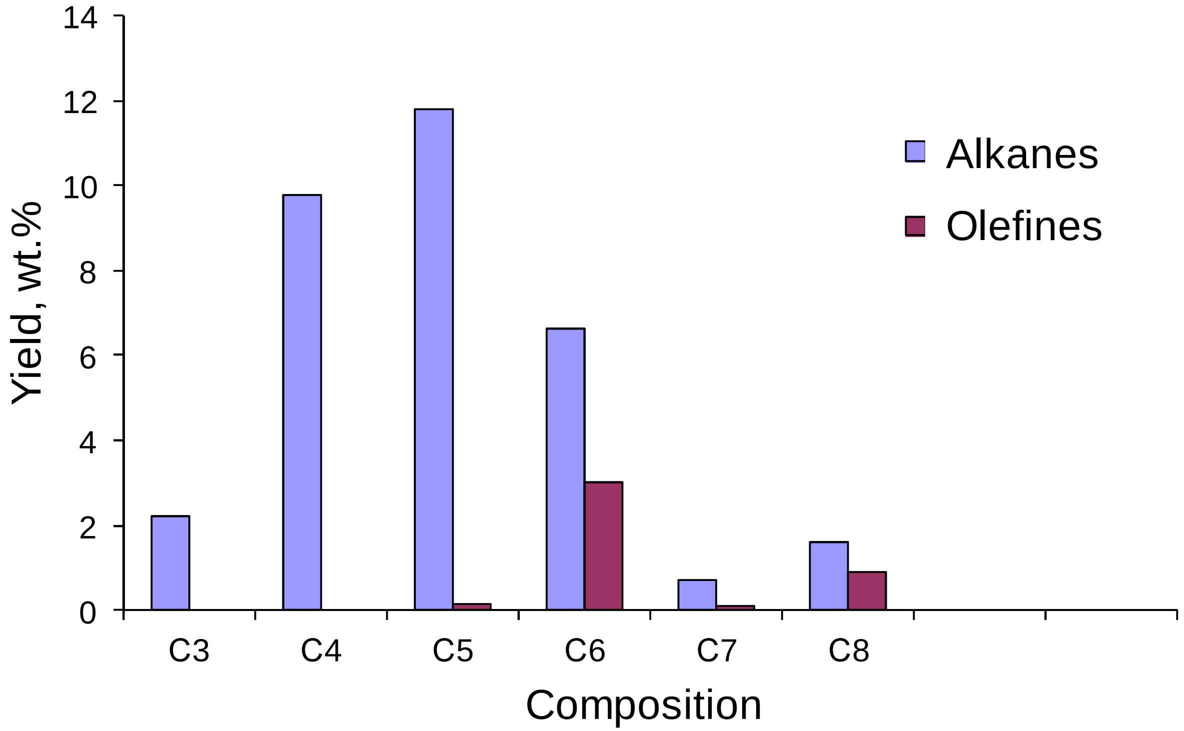
T=350ºC, Ar

Effect of precursor (mono- and hetero-metallic complexes)





Conversion of alcohols mixture (C_2-C_5)



T=350°C, Ar

Fe_2O_3-MgO/Al_2O_3+Pt/Al_2O_3

Feed composition	
Ethanol	80%
Propanol	5%
Butanol	5%
Isoamyl alcohol	10%

- ~40% of alkanes (C_4-C_8).
- ~60% molecules with non-linear structure.

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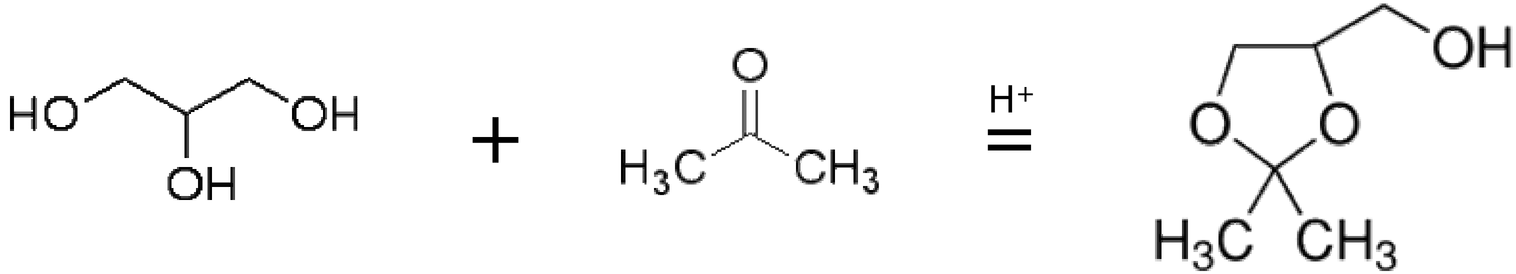
Octane number buster: solketal

Ketalization of glycerin

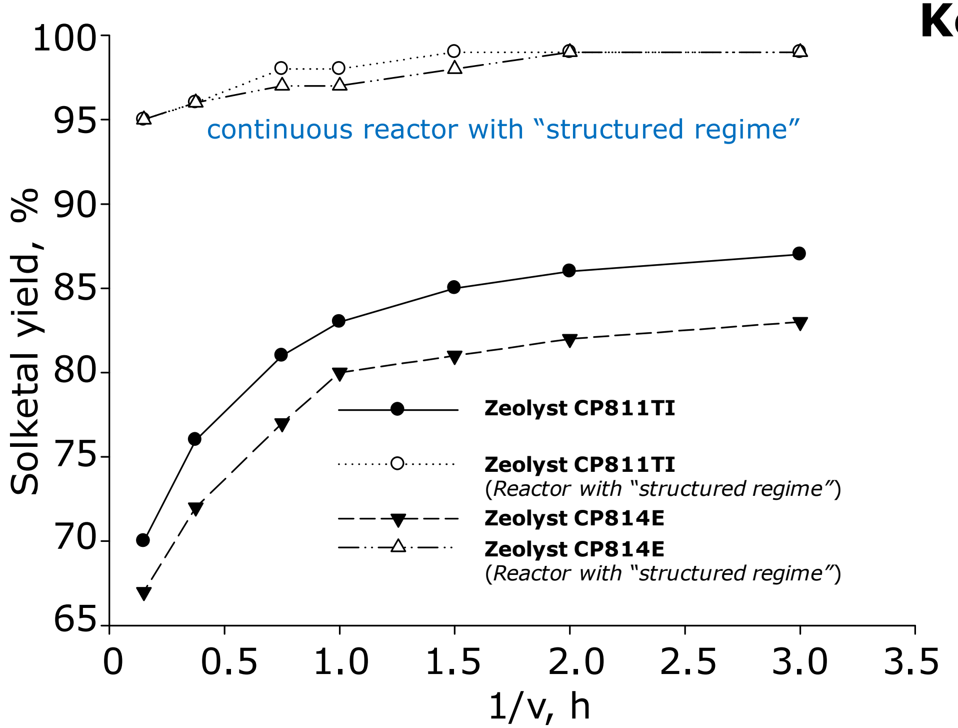


- By-product in *bio*diesel production (*~100 kg per 1 ton of biodiesel*)
- Poor mixing with gasoline (*hydrophilic nature: $logK_{ow}$=-1.76*)

- By-product of large-scale petrochemical processes (*excess on the market*)
- Poor mixing with gasoline (*hydrophilic nature: $logK_{ow}$=-0.24*)

- Increasing of octane number
- Reduction of gum formation (*good for gasoline from CC with high olefin content*)
- Good mixing with gasoline (*hydrophobic nature: $logK_{ow}$=1.07*)

Solketal synthesis: continuous reactor + zeolite



Ketalization is reversible reaction!

Increasing of conversion by:

- Continuous removal of water (distillation cannot be used).
  Solution: membrane
  (but still not so effective).
- Selection of catalysts.
  Solution: zeolites.
- Excess of substrate (acetone) in the feed.
  Solution: local increasing of acetone:glycerin ratio (like in alkylation process).

New ketalization process developed by TIPS RAS:

- continuous reactor with "structured regime"
- zeolite-based catalyst
- acetone:glycerin = 6:1
- $T_{reaction}$=25-40°C

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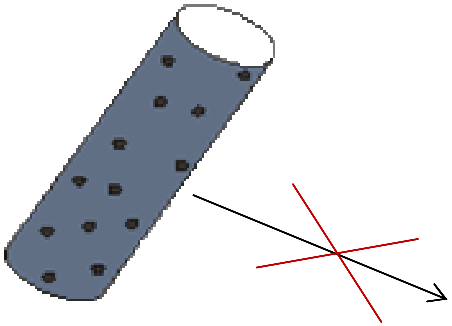
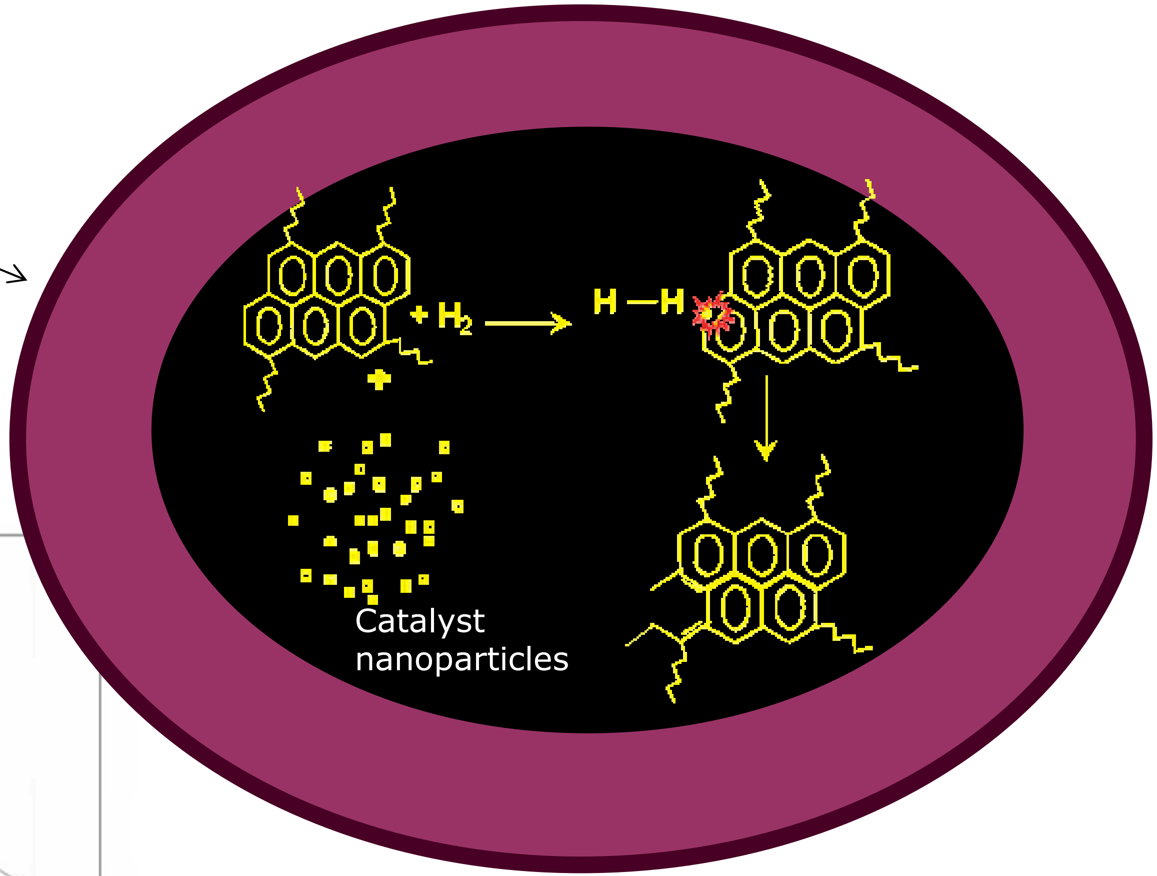
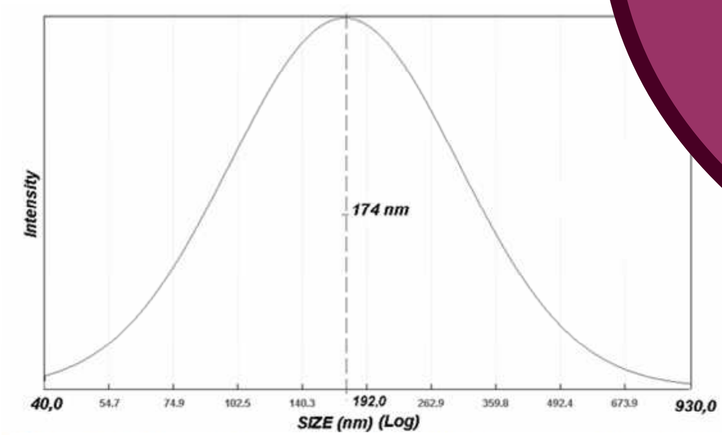
Thermo-catalytic processing: concept of novel heavy residual hydroconversion

Traditional catalyst







Size distribution of catalytic particles

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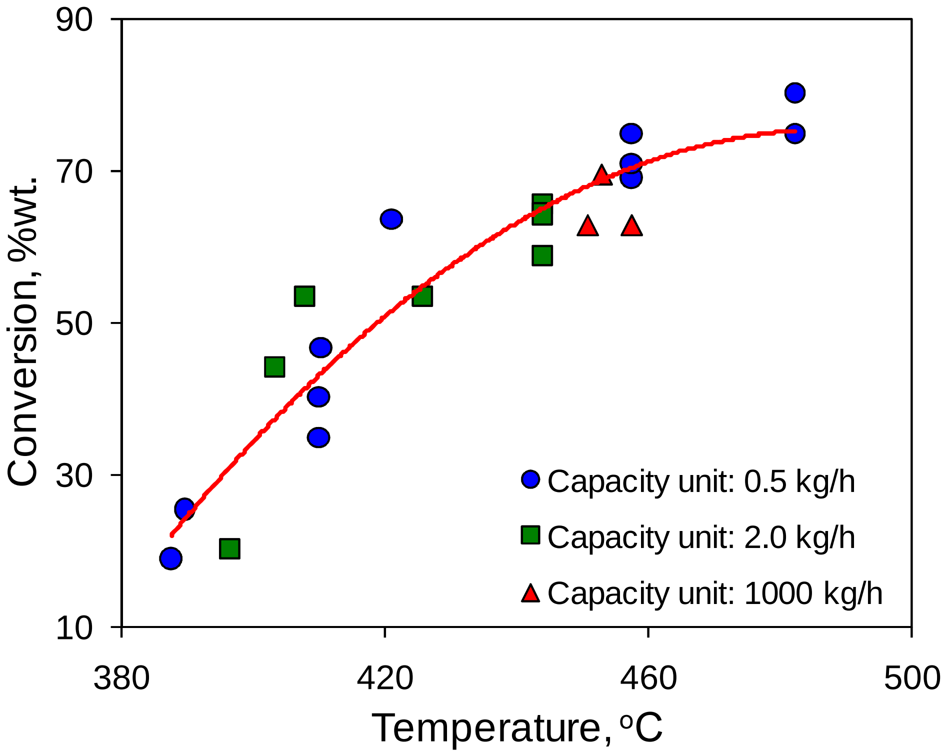
Scaling up of heavy residual hydroconversion technology



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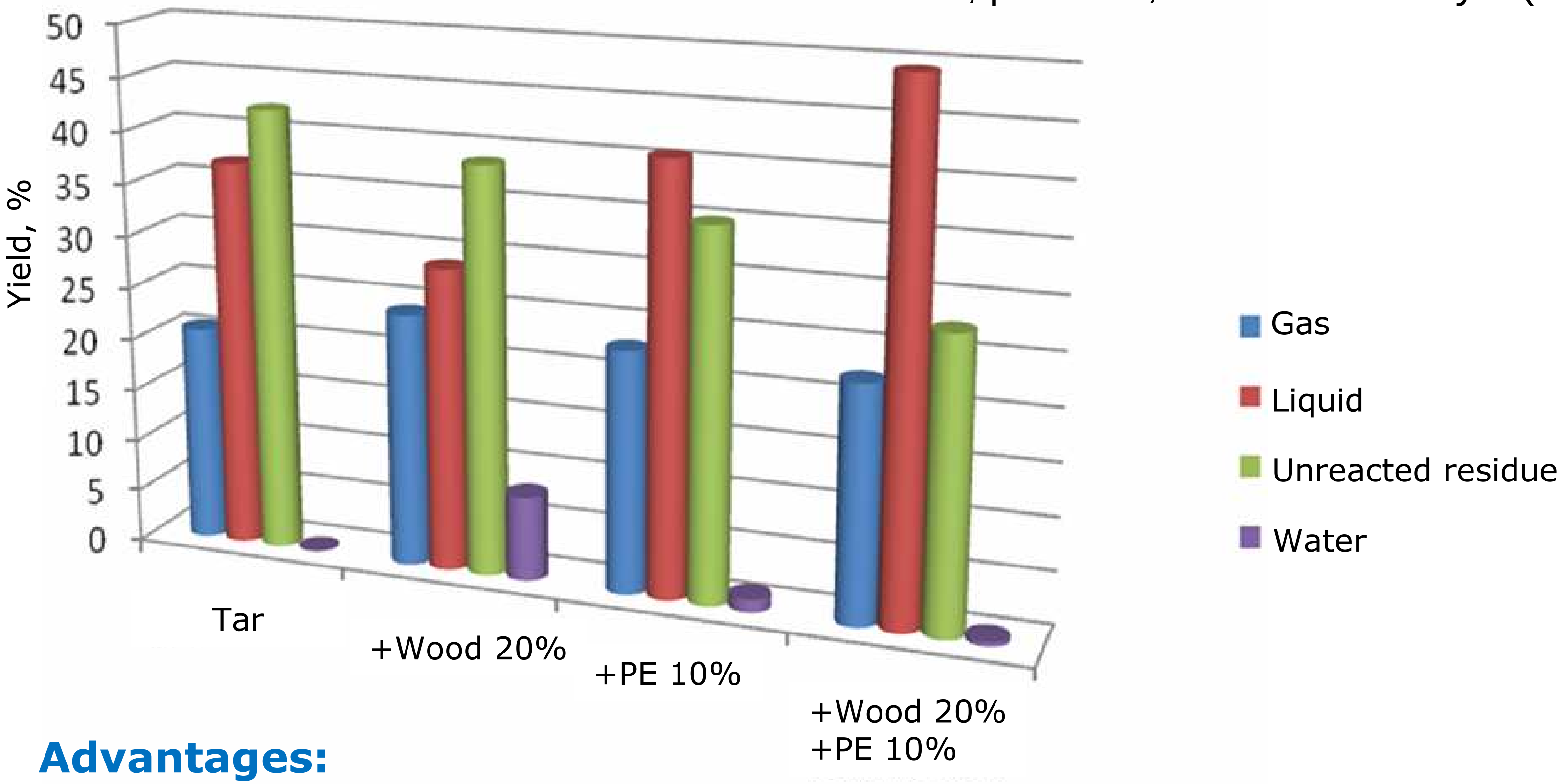
Tar conversion with wood and polymer wastes

T=450°C, p=7MPa, Mo-based catalyst (0.05%)



Advantages:

- Wood waste fraction can be increased up to 50% (or even higher after modification of mixing unit).
- Lignin is not a problem in this process.
- Nano-sized catalyst is recycled with unreacted residue.

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Summary

- Biorefinery is the future of downstream industry.
- Renewable feedstock can be used at existing refineries and chemical plants (after some process improvements).
- Wide range of valuable products can be produced from biomass and polymer wastes.

THANK YOU FOR YOUR ATTENTION!!!

Alexey Volkov

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