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Department of Energy Process Engineering and Chemical Engineering

Synthesis Routes via Methanol and DME

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Outline

- Introduction
- Methanol-Synthesis
- DME-Synthesis
- Fuel Syntheses Routes
  - Diesel
  - Gasoline
  - Project Examples in Germany
  - Comparison
- Example for Economic and Ecologic calculations
- Conclusion

Introduction

Methanol

STD

STF

TIGAS

DTG

Dimethyl ether

STG

MOGD

MTS

DTO

MTG

MTO

MTD

- Various processes → differences/ similarities?
- Goal of this presentation: well arranged structure, classification.

Introduction

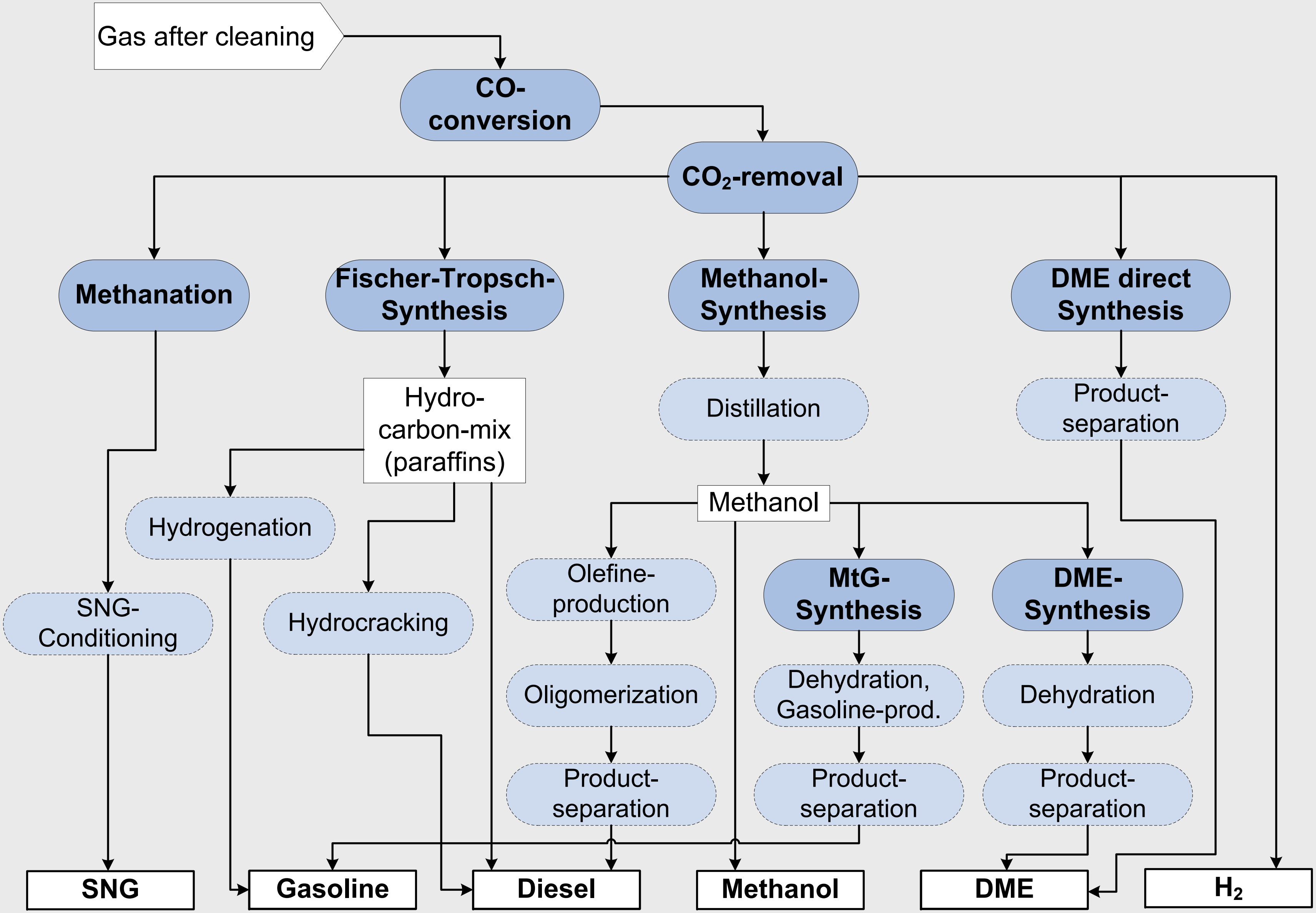
Why Methanol and DME?

- Methanol suitable as fuel.
- Methanol is basis for different processes: chemical feedstock, fuel synthesis, …
- DME also suitable for direct use in engines.
- DME as intermediate in syntheses from methanol to fuels.

Properties:

	Gasoline	**Diesel**	**Methanol**	**DME**	**SNG**
Chem. formula	$\approx C_7H_{16}$	$\approx C_{14}H_{30}$	CH_3OH	CH_3OCH_3	$\approx CH_4$
Molar mass (g/mol)	100,2	198,4	32,04	45,07	16,04
Density (kg/m³)	737	856	792	661	0,72
Boiling point/ -range (°C)	38-204	125-400	64	-24,9	-162
LHV (MJ/kg)	43,47	41,66	19,99	28,62	47,79

Introduction



Gas after cleaning

CO-conversion

CO_2-removal

Methanation

Fischer-Tropsch-Synthesis

Methanol-Synthesis

DME direct Synthesis

Hydro-carbon-mix (paraffins)

Distillation

Product-separation

Methanol

Hydrogenation

SNG-Conditioning

Hydrocracking

Olefine-production

MtG-Synthesis

DME-Synthesis

Oligomerization

Dehydration, Gasoline-prod.

Dehydration

Product-separation

Product-separation

Product-separation

SNG

Gasoline

Diesel

Methanol

DME

H_2

Introduction

- **Requirements of syntheses to synthesis gas:**
  - Methanol-Synthesis:
    - Sulfur < 0,1 ppm
    - $(H_2\text{-}CO_2)/(CO+CO_2) \approx 2$
  - DME (direct Synthesis):
    - Sulfur < 0,1 ppm
    - $H_2/CO \approx 1$
  - Fischer-Tropsch-Synthesis:
    - $H_2S + COS + CS_2 < 1$ ppm
    - $H_2/CO \approx 2$
  - Methanation:
    - $H_2S < 0,1$ ppm
    - $H_2/(3CO + 4CO_2) \approx 1$

- **H_2/CO-ratio in rawgas:**
  - Carbo-V, Choren: 0,9
  - bioliq, KIT: 0,5
  - FICFB Güssing: 1,7
  - DWS, IEC Freiberg: 1,1

  - General:
    - Fixed Bed: 3
    - Fluidized Bed: 1…2
    - Entrained Flow: 0,5

→ syngas-yield also of relevance

Methanol-Synthesis

Chemistry:

Syngas → Methanol

- $CO + 2H_2 \rightarrow CH_3OH$ $\Delta H_{298K} = -92$ kJ/mol
  $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta H_{298K} = -50$ kJ/mol
  $CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H_{298K} = 41$ kJ/mol
- Byproducts: higher alcohols, hydrocarbons, esters, DME, ketones
- Catalysts: **Cu** / ZnO / Al_2O_3
- MeOH-yield: once through: 25 % / with recycle: > 99 %
- Exothermic reactions → optional steam generation

Process conditions:

- $$\frac{H_2\text{-}CO_2}{CO+CO_2} = 2 \quad (2{,}05 – 2{,}1)$$
- Classification process conditions:
  - High pressure: 25 – 30 MPa
  - Medium pressure: 10 – 25 MPa
  - **Low pressure: 5 – 10 MPa**

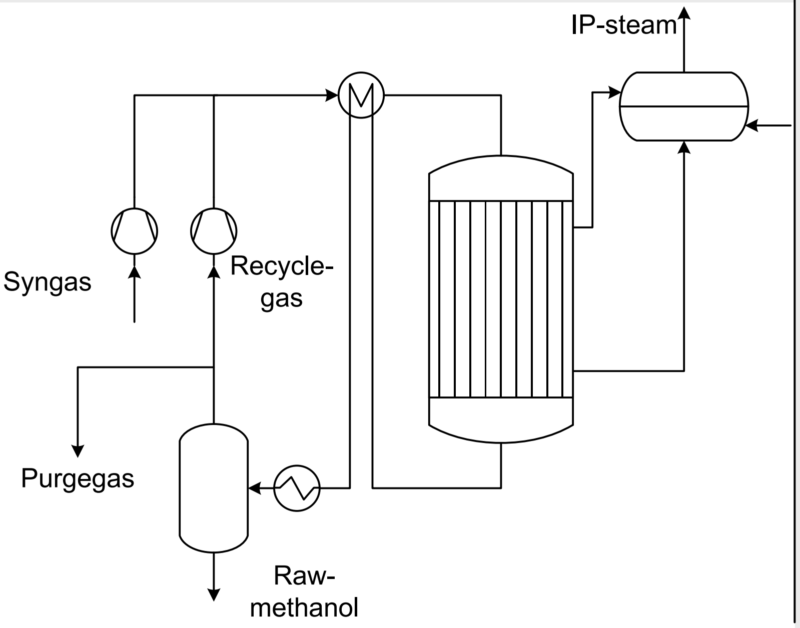
Advantage Low pressure processes: lower invest- and operating costs, availability, high flexibility regarding plant capacity.

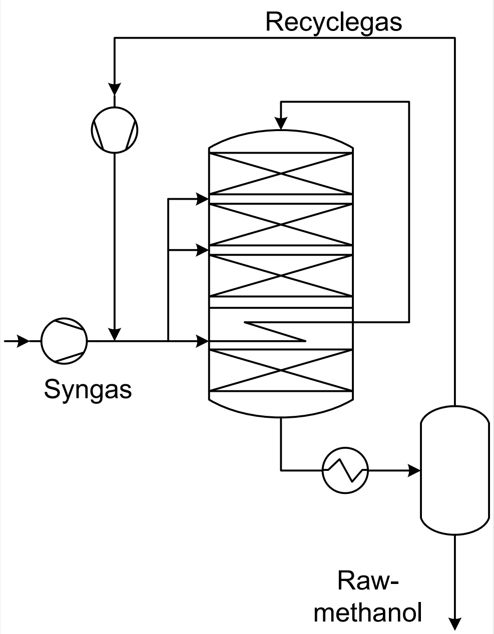
Methanol-Synthesis

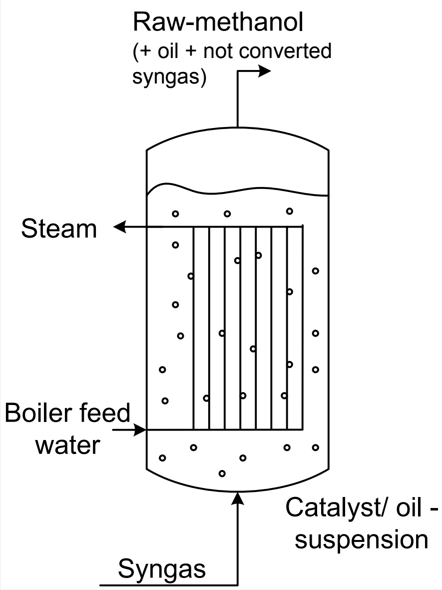
Reactor design:

Syngas → Methanol

	Isothermal	Adiabatic	Liquid Phase
Example	Lurgi-type	ICI	LPMeOH™
Market share	> 60 %	30 %	Pilot plant
Catalyst	Cu / ZnO / Cr_2O_3	Cu / ZnO / Al_2O_3	Powdery Cu / ZnO in oil
Temperature	230 – 265 °C	270 °C	250 °C
Pressure	60 – 80 bar	50 – 100 bar	85 bar







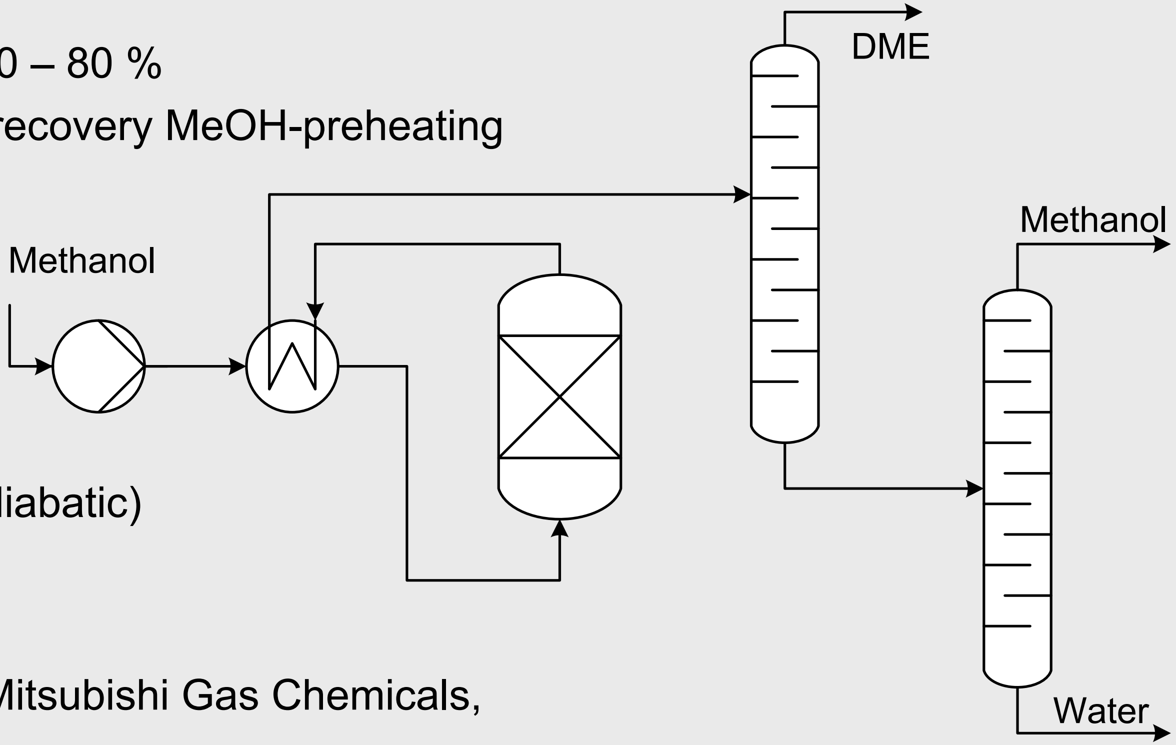
DME-Synthesis

Methanol-to-DME (MTD)

Syngas → Methanol $\xrightarrow{\text{MTD}}$ DME

Chemistry:

- $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H_{298K} = -23$ kJ/mol
- Catalysts: γAl_2O_3, Zeolite
- DME-yield: once through: 70 – 80 %
- Exothermic reactions → heat recovery MeOH-preheating



Process conditions:

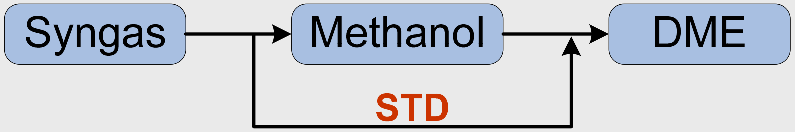
- Simple process
- Pressure: 10 – 25 bar
- Temperature: 250 °C (inlet, adiabatic)

Granter of licence:

- Lurgi, Uhde, Haldor-Topsoe, Mitsubishi Gas Chemicals, Toyo Eng. Corp.

DME-Synthesis

Syngas-to-DME (STD)

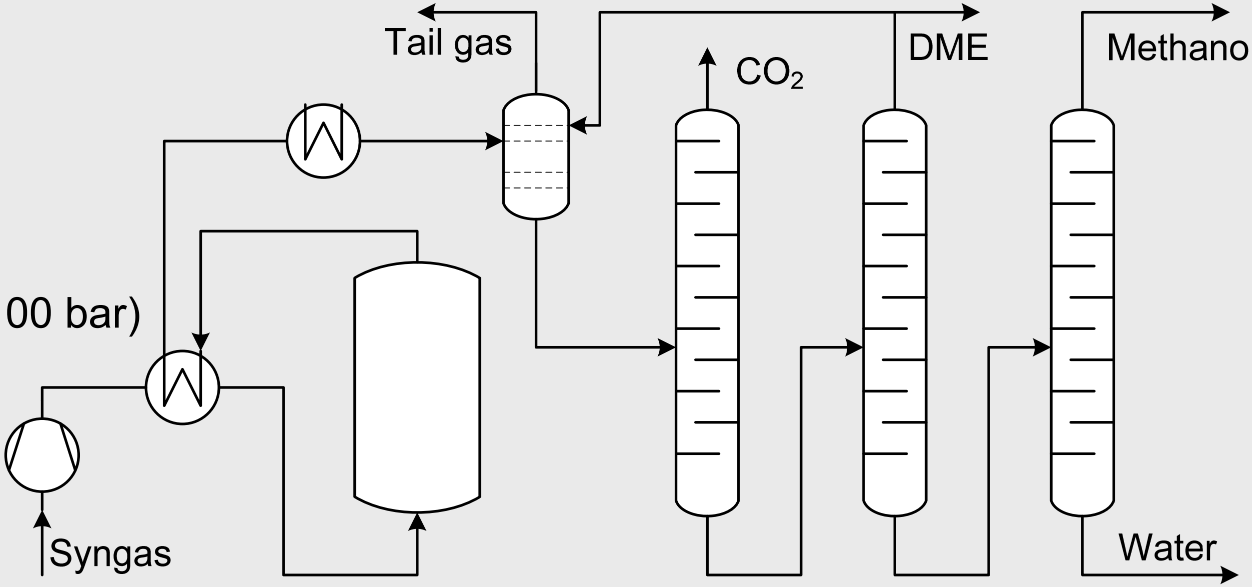


Chemistry:

- $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$ $\Delta H_{298K} = -246$ kJ/mol
- Catalysts: γAl_2O_3, Zeolite
- DME-yield: once through: 33 – 50 %
- Strong exothermic reaction → feed-preheating, steam generation

Process conditions:

- $\frac{H_2}{CO} = 1$ (0,7 – 1)
- Pressure: 30 – 70 bar (100 bar)
- Temperature: 250 – 280 °C

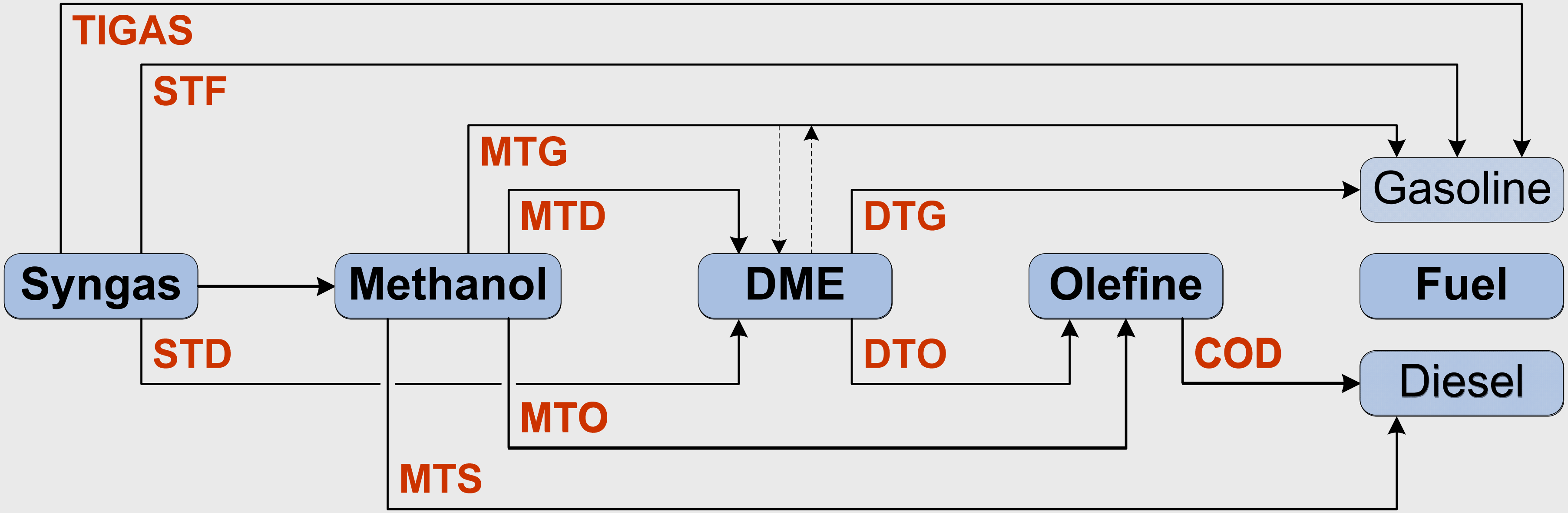


Granter of licence:

- JFE Holdings, Inc., Air Products and Chemicals, Haldor-Topsoe

Fuel Syntheses Routes

Overview of different fuel syntheses



TIGAS = Topsoe Integrated Gasoline Synthesis
MTG = Methanol-to-Gasoline (ExxonMobil, Uhde)
DTG = Dimethyl ether-to-Gasoline (z.B. KIT)
DTO = Dimethyl ether-to-Olefins (z.B. KIT)
MTO = Methanol-to-Olefins (z.B. UOP)

STF = Syngas-to-Fuel (CAC, TU BAF)
MTD = Methanol-to-Dimethyl ether (z.B. Lurgi)
STD = Syngas-to-Dimethyl ether (z.B. JFE)
COD = Conversion of Olefins to Distillates (z.B. Lurgi)
MTS = MtSynfuels® (Lurgi)

Fuel Syntheses Routes - Diesel

Methanol-to-Olefins (MTO) – Conversion of Olefins to Distillates (COD)

Chemistry:

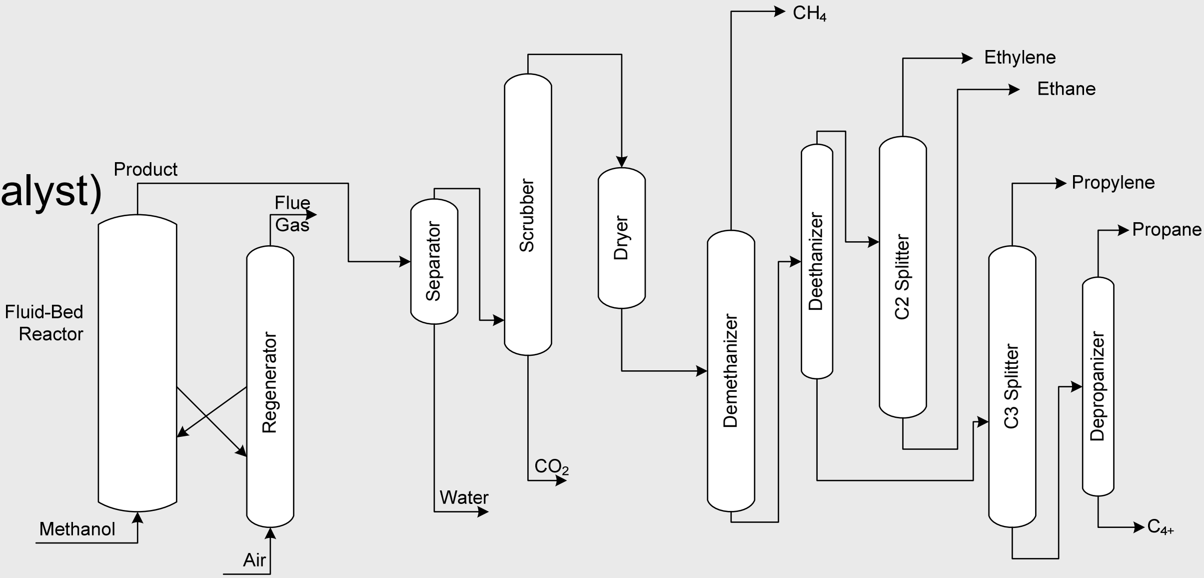
- $2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O \leftrightarrow (CH_2)_2 + 2\ H_2O$ $\Delta H_{298K} = -24$ kJ/mol
- $CH_3OCH_3 \rightarrow (CH_2)_2 + H_2O$ $\Delta H_{298K} = -19$ kJ/mol
- Catalyst: Zeolite (SAPO-34 – Si, Al, P)
- Product-yield: ethylene (48 %) and propylene (33 %)

Process conditions:

- Two fluidized bed reactors (one for regeneration of the catalyst)
- Temperature: 400 – 450 °C
- 5 separation steps

Granter of licence:

- UOP/Hydro
- Other: Lurgi, Japan DME Ltd.



Fuel Syntheses Routes - Diesel

Methanol-to-Olefins (MTO) – Conversion of Olefins to Distillates (COD)

Chemistry:

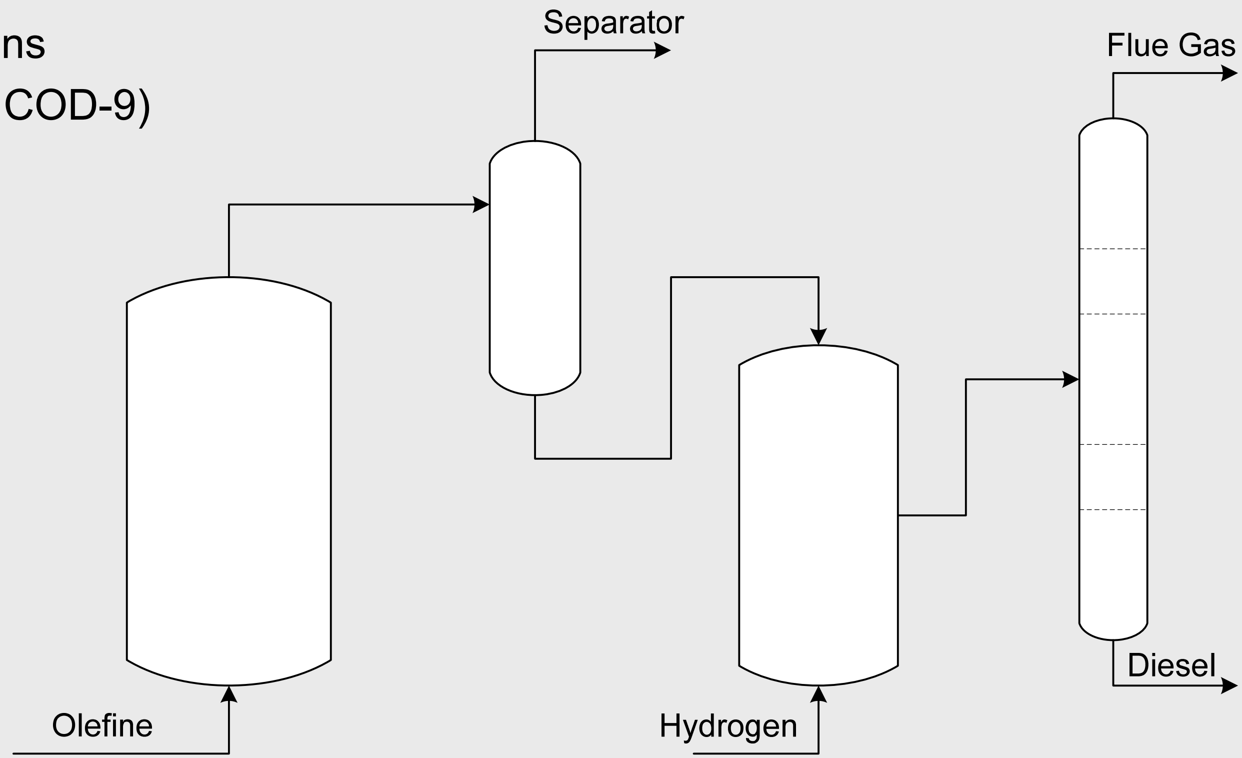
- Oligomerization of the olefins
- Catalyst: Zeolite (z.B. COD-9)

Process conditions:

- Temperature: < 280 °C
- Pressure: 55 bar

Granter of licence:

- Lurgi



Plants in operation:

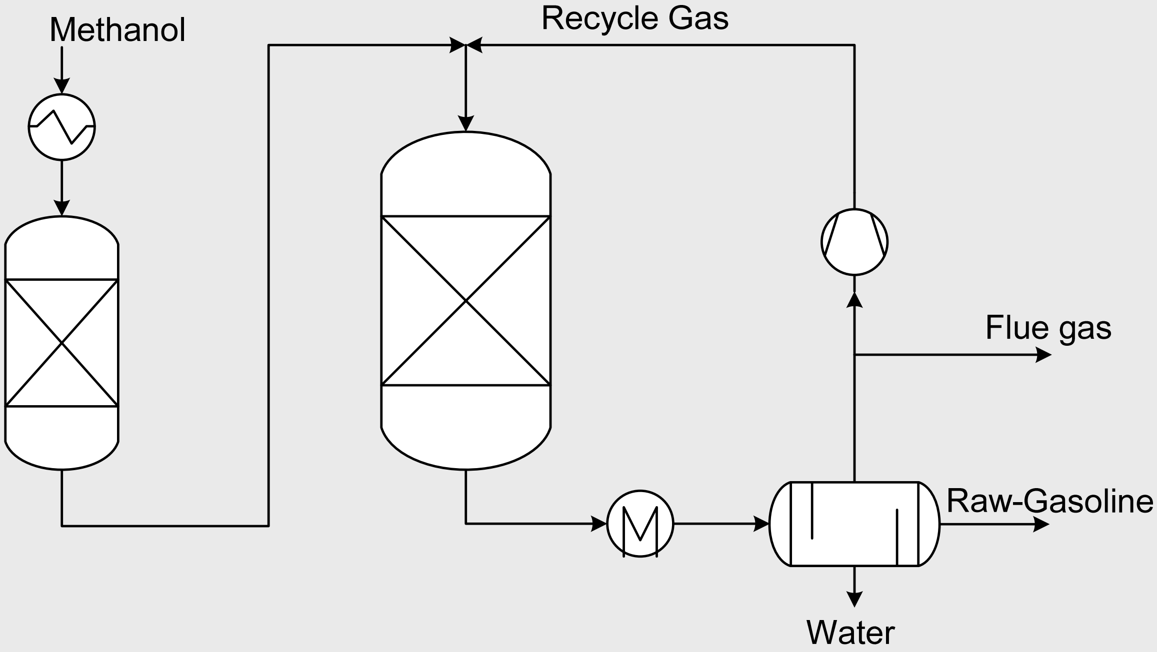
- South Africa, Mossgas, oligomerization of light olefins from Fischer-Tropsch plant

Fuel Syntheses Routes - Gasoline

Methanol-to-Gasoline (MTG)

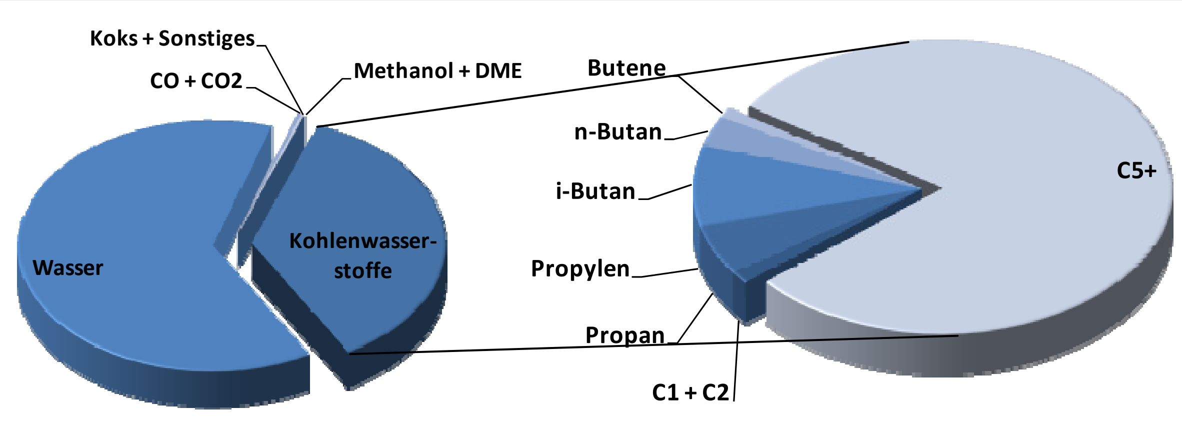
Chemistry:

- $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
  $CH_3OCH_3 \rightarrow (-CH_2-)_2 + H_2O$
  $\Delta H_{298K} =$ -23 kJ/mol
- HC-yield: 44 wt.-%
- Strong exothermic reaction



Process conditions:

- <u>1. Dehydration of methanol</u>
  Pressure: 14 – 24 bar
  Temperature: 315 – 400 °C
  Catalyst: Al_2O_3
- <u>2. Gasoline production</u>
  Pressure: 14 – 24 bar
  Temperature: 340 – 450 °C
  Catalyst: Zeolite



Granter of licence:

- ExxonMobil, Uhde

Fuel Syntheses Routes - Gasoline

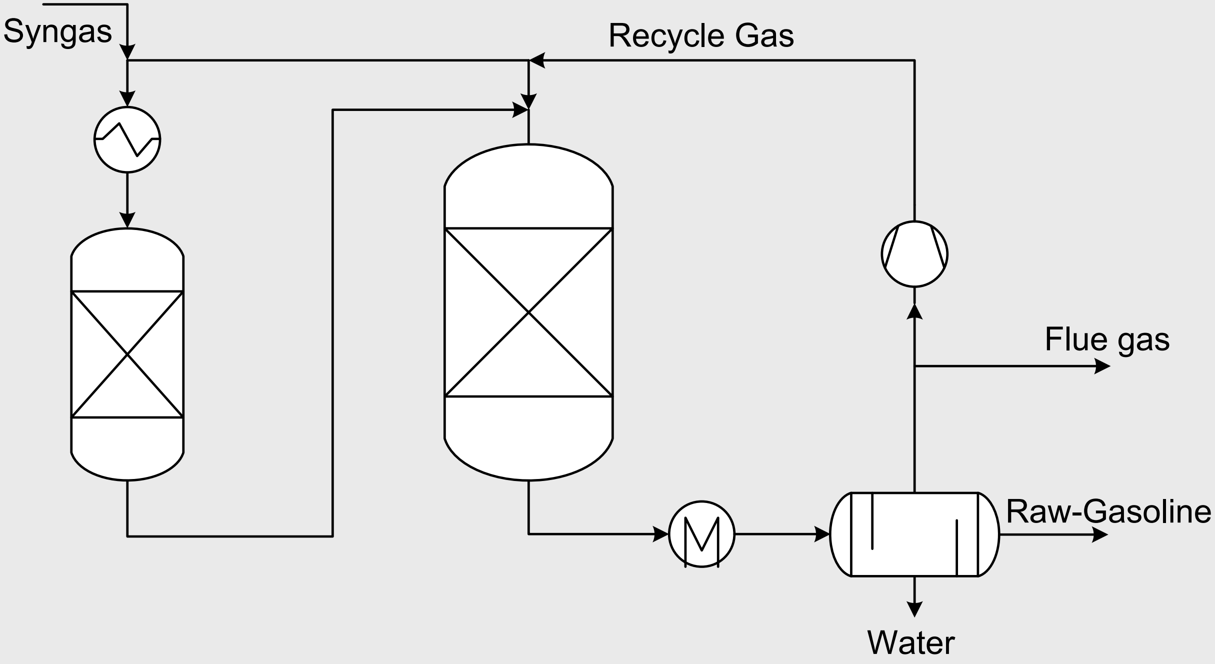
Topsøe Integrated Gasoline Synthesis (TIGAS)

Chemistry:

- Coupling MeOH + MTG synthesis

Process conditions:

- 1. MeOH/DME production
  Pressure: 40 – 60 bar
  Temperature: 240 – 290 °C
  Catalyst: bifunctional
- 2. Gasoline production
  Pressure: 40 – 60 bar
  Temperature: 360 – 420 °C
  Catalyst: Zeolite



Granter of licence:

- Haldor-Topsøe

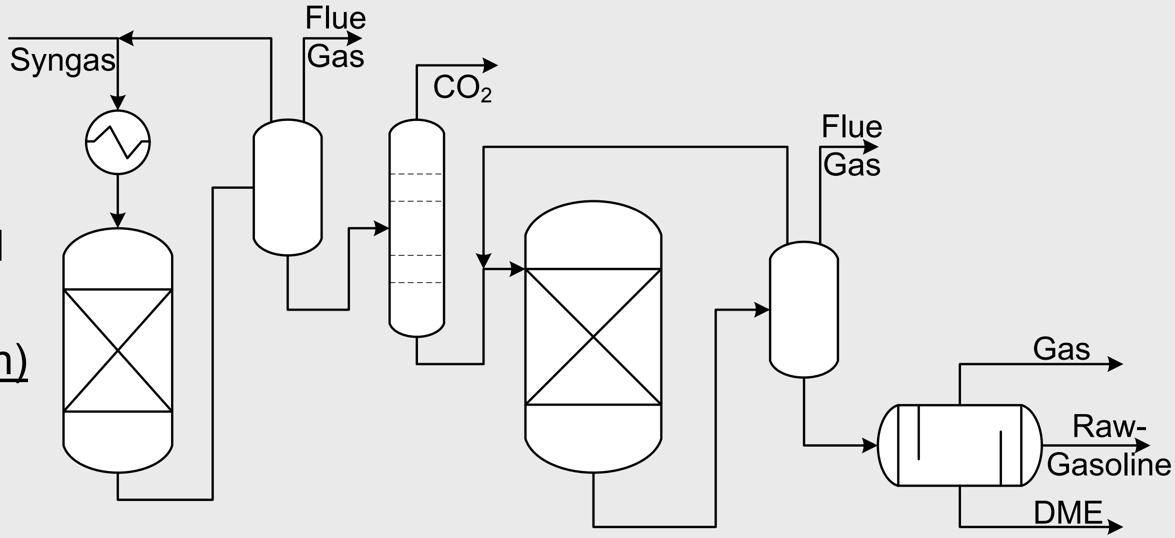
Fuel Syntheses Routes - Project Examples in Germany

Syngas-to-Dimethyl ether (STD),
Dimethyl ether-to-Gasoline (DTG)

Chemistry:

- $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$ $\Delta H_{298K} = -246$ kJ/mol
  $CH_3OCH_3 \rightarrow (-CH_2-)_2 + H_2O$
- Strong exothermic reaction
  → feed-preheating, steam generation

Process conditions:



- 1. DME production (≈ 150 kg/h)
  Pressure: up to 60 bar
  Temperature: 250 °C, isothermal
  Catalyst: bifunctional
- 2. Gasoline production (≈ 80 kg/h)
  Pressure: 25 bar
  Temperature: 350 – 450 °C
  Catalyst: Zeolite

Place of erection:

- Karlsruhe Institute of Technology (KIT), bioliq®

Fuel Syntheses Routes - Project Examples in Germany

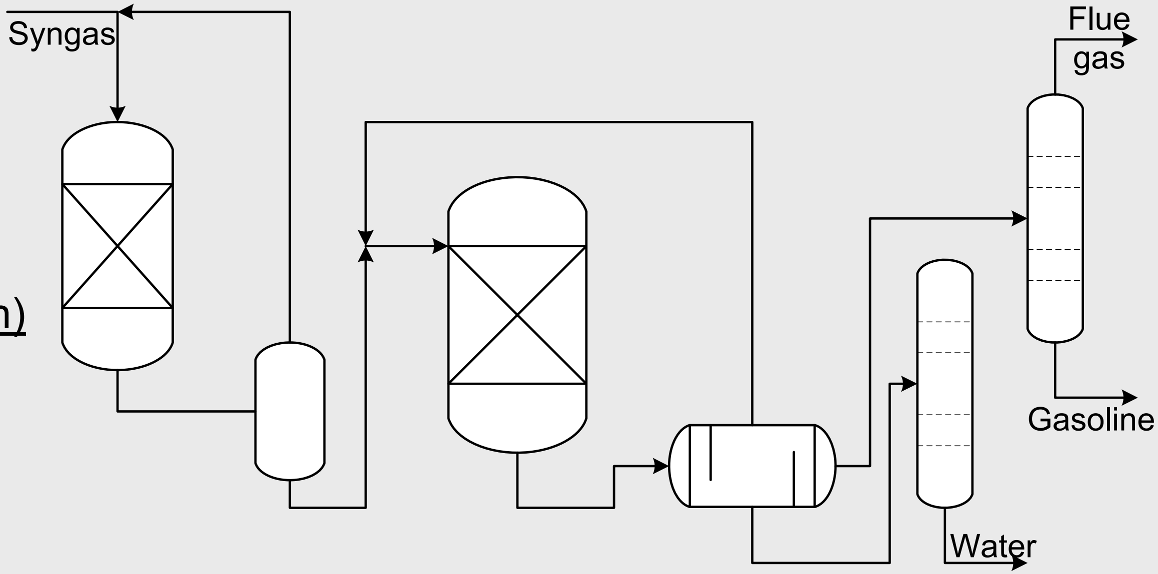
Syngas-to-Fuel (STF)

Chemistry:

- $CO + 2H_2 \rightarrow CH_3OH$ $\Delta H_{298K} = -92$ kJ/mol
  $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta H_{298K} = -50$ kJ/mol
  $CH_3OH \rightarrow (-CH_2-) + H_2O$

Process conditions:

- 1. MeOH production
  Pressure: 40 – 60 bar
  Temperature: 240 – 290 °C
- 2. Gasoline production (≈ 80 kg/h)
  Pressure: 5 – 15 bar
  Temperature: 360 – 410 °C



Place of erection:

- TU Bergakademie Freiberg, IEC

Fuel Syntheses Routes - Project Examples in Germany

Pictures STF plant

Location: Freiberg, Reiche Zeche

Fuel Syntheses Routes - Comparison

Pre-stages

	MeOH	MTD	STD
Pressure (bar)	50 – 100	10 – 25	30 – 100
Temperature (°C)	230 – 270	250	210 – 290
Number of reactors[1]	1	2	1
Catalyst	Cu, ZnO, Cr_2O_3, Al_2O_3	Al_2O_3, Zeolite	Cu, Al_2O_3, Zeolite
H_2/CO	2	2	1
Product	MeOH	DME	DME
Stage of development	commercial plant	pilot plant	pilot plant

[1] Number of reactors starting with syngas

Fuel Syntheses Routes - Comparison

Fuel Syntheses

	MTO-COD	MeOH-MtG	TIGAS	STD-DTG	STF
Pressure (bar)	60 / 55	14 – 24	40 – 60	60 / 25	40 – 60 / 5 – 15
Temperature (°C)	400 / 280	315 – 450	240 – 420	250 / 350 – 450	240 – 290 / 360 – 410
Number of reactors[1]	4	3	2	2	2
Catalyst	Zeolite	Al_2O_3, Zeolite	Bifunct., Zeolite	Bifunct., Zeolite	
H_2/CO	2	2	1	1	2
Product	Diesel	Gasoline	Gasoline	Gasoline	Gasoline
Stage of development	commercial plant	commercial plant	pilot plant	planned	start-up

[1] Number of reactors starting with syngas

Example for Economic and Ecologic calculations

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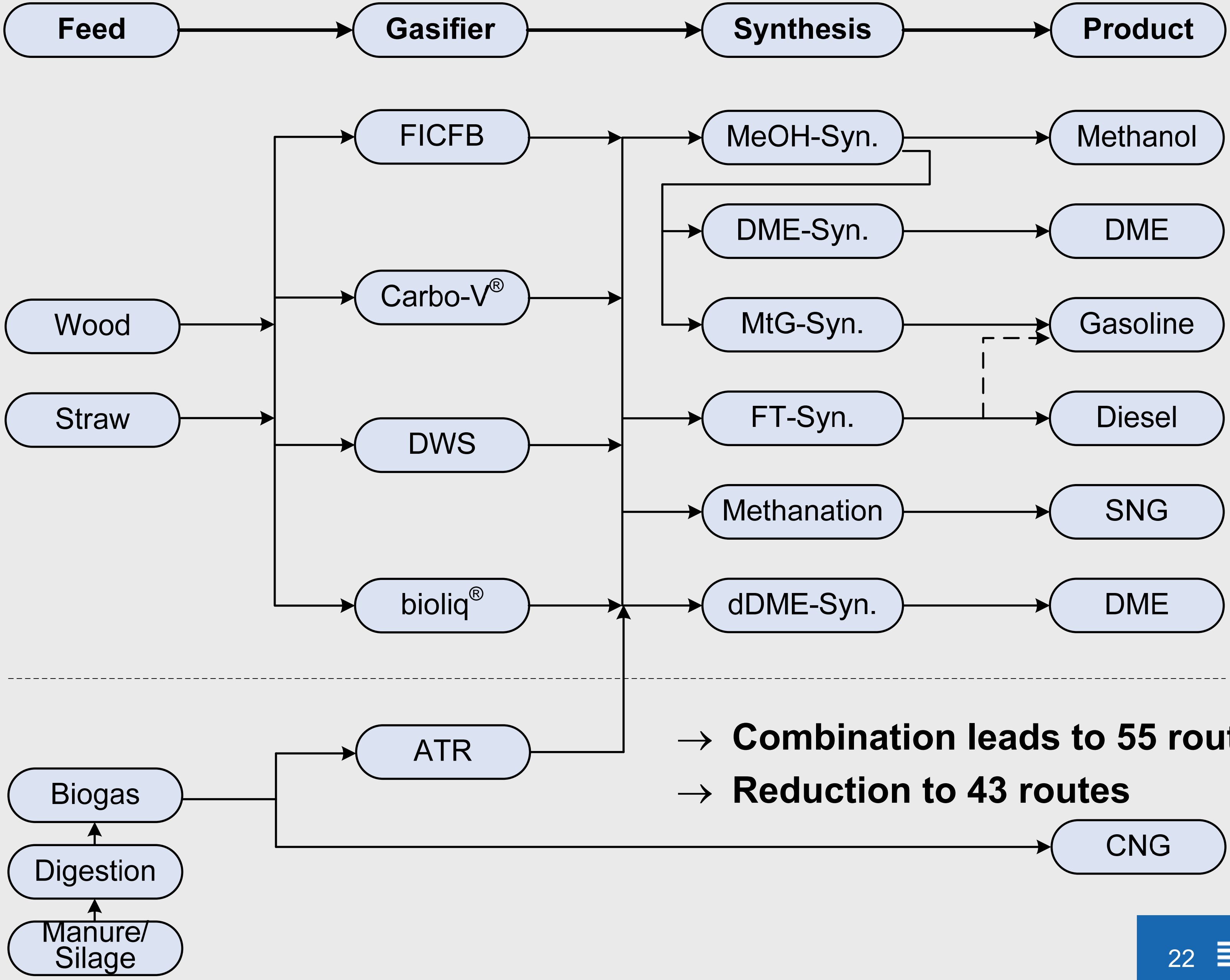
Abschlussbericht

Ermittlung spezifizierter Kosten und ökologischer Auswirkungen der Erzeugung von BtL-Kraftstoffen und Biogas

Kurztitel: Spezifizierte BtL-Kraftstoffkosten

Gefördert durch das Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (BMELV)

Example for Economic and Ecologic calculations



Feed → **Gasifier** → **Synthesis** → **Product**

FICFB

MeOH-Syn.

Methanol

DME-Syn.

DME

Carbo-V®

Wood

MtG-Syn.

Gasoline

Straw

FT-Syn.

Diesel

DWS

Methanation

SNG

bioliq®

dDME-Syn.

DME

ATR

Biogas

Digestion

Manure/ Silage

CNG

→ **Combination leads to 55 routes!**

→ **Reduction to 43 routes**

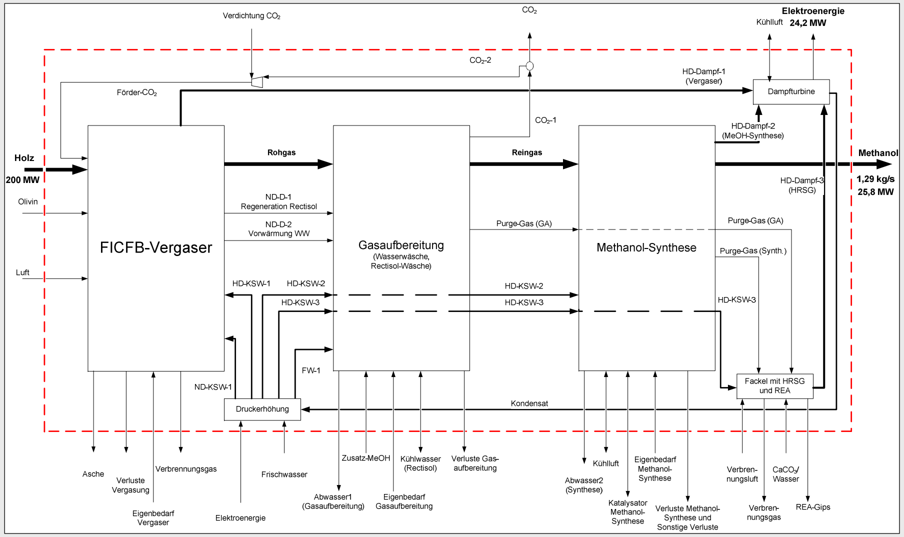
Example for Economic and Ecologic calculations

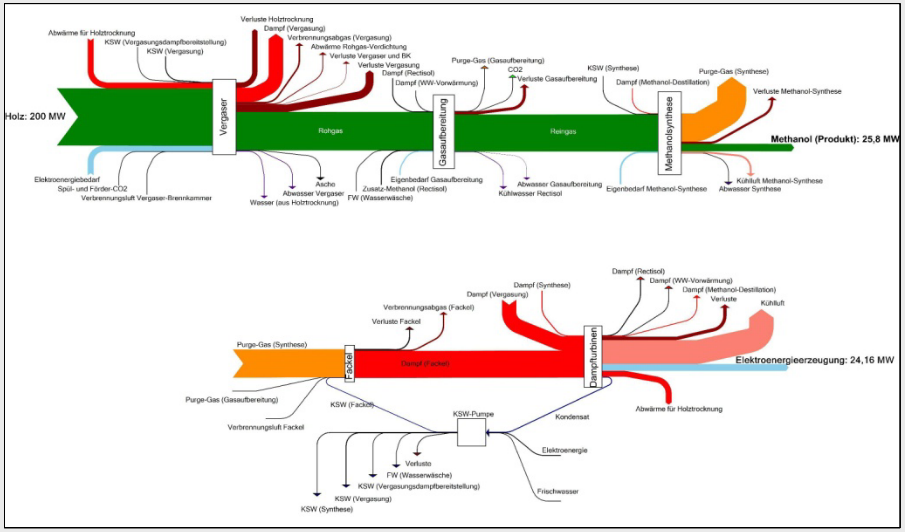
Method:

- Detailed modeling of all 43 routes with ASPENplus™
- gas cleaning, gas processing and auxiliary systems identical
  - Filter, wet scrubber, Rectisol + clean gas shift → due to necessity
- High degree of thermal process integration → steam cycles
- Steam turbines for power generation

Results:

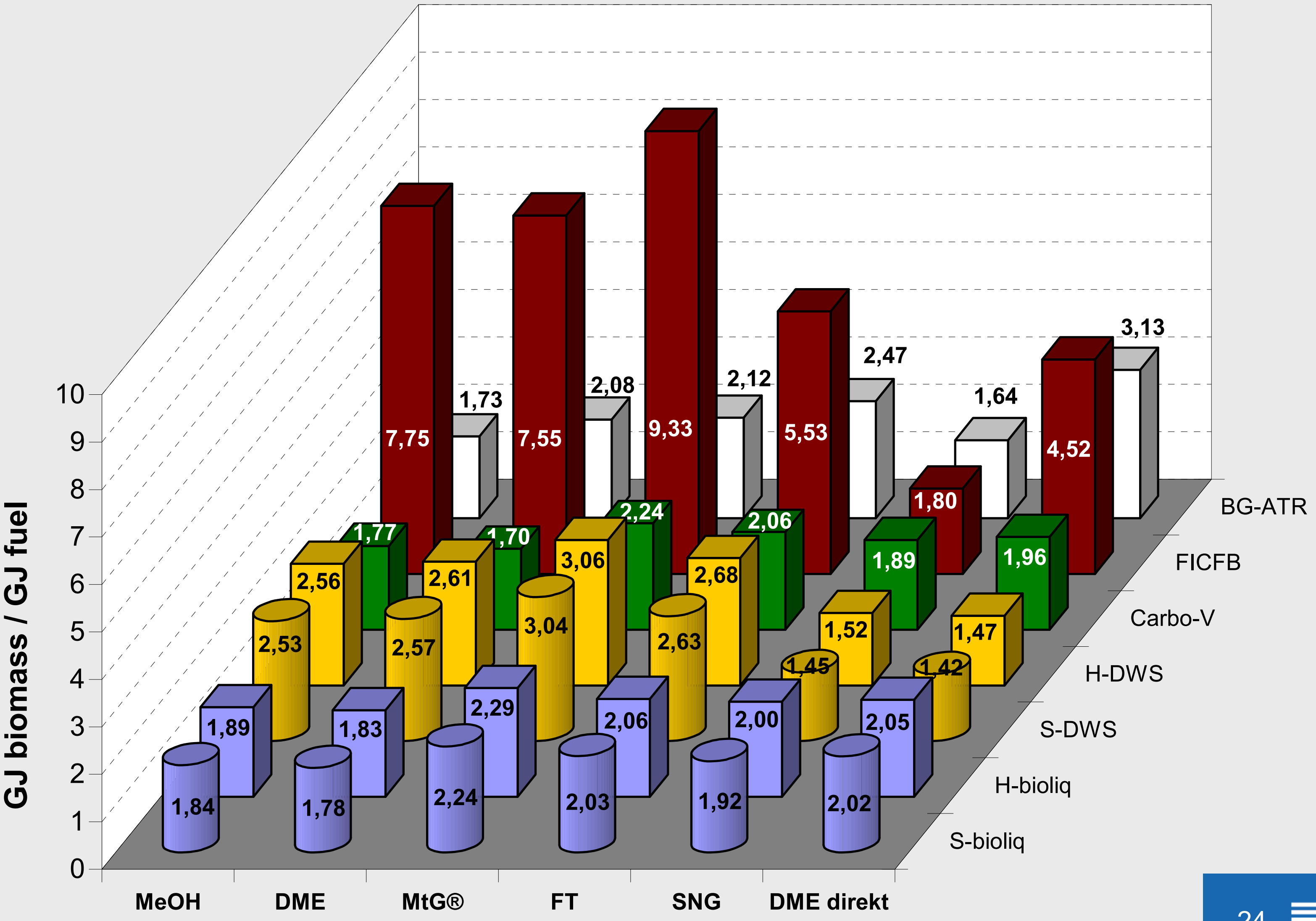
- Fuel production (kg/s, MW)
- Consumption of resources (ha/GJ, t/GJ, GJ/GJ)
- Power generation / consumption (kWh/GJ)
- Waste heat (GJ/GJ)
- Overall efficiency





Example for Economic and Ecologic calculations

- Example: Consumption of resources

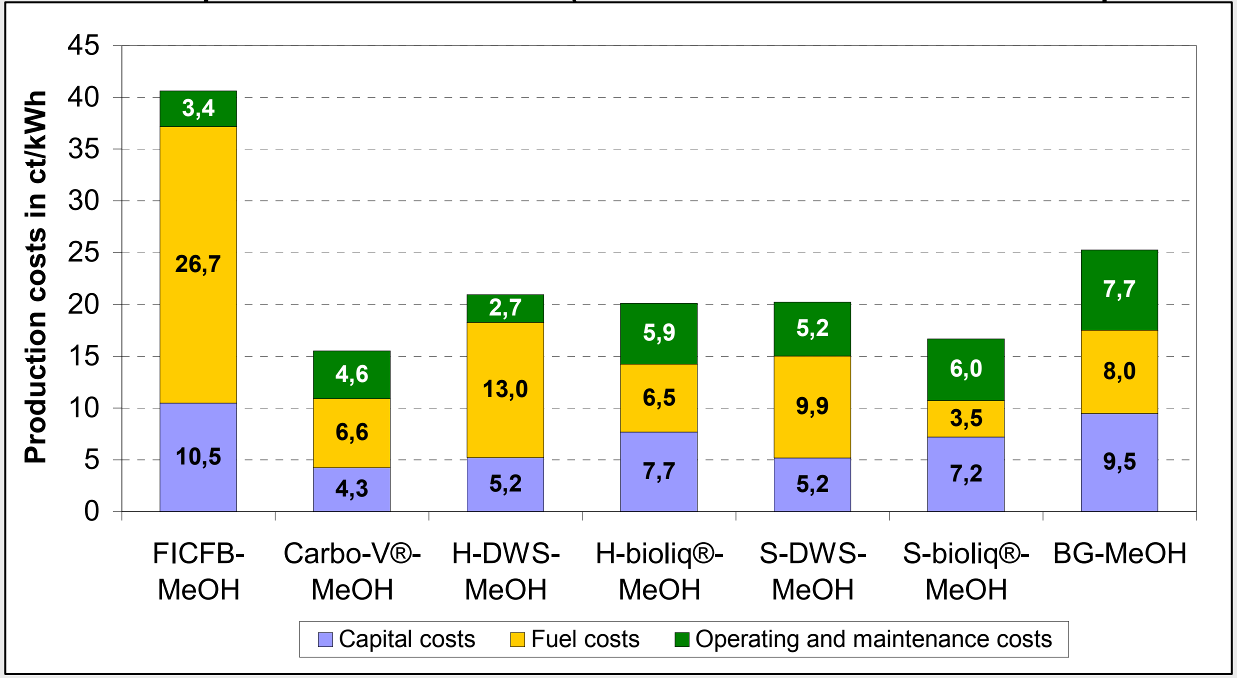


Example for Economic and Ecologic calculations

- Results for standard scenario:

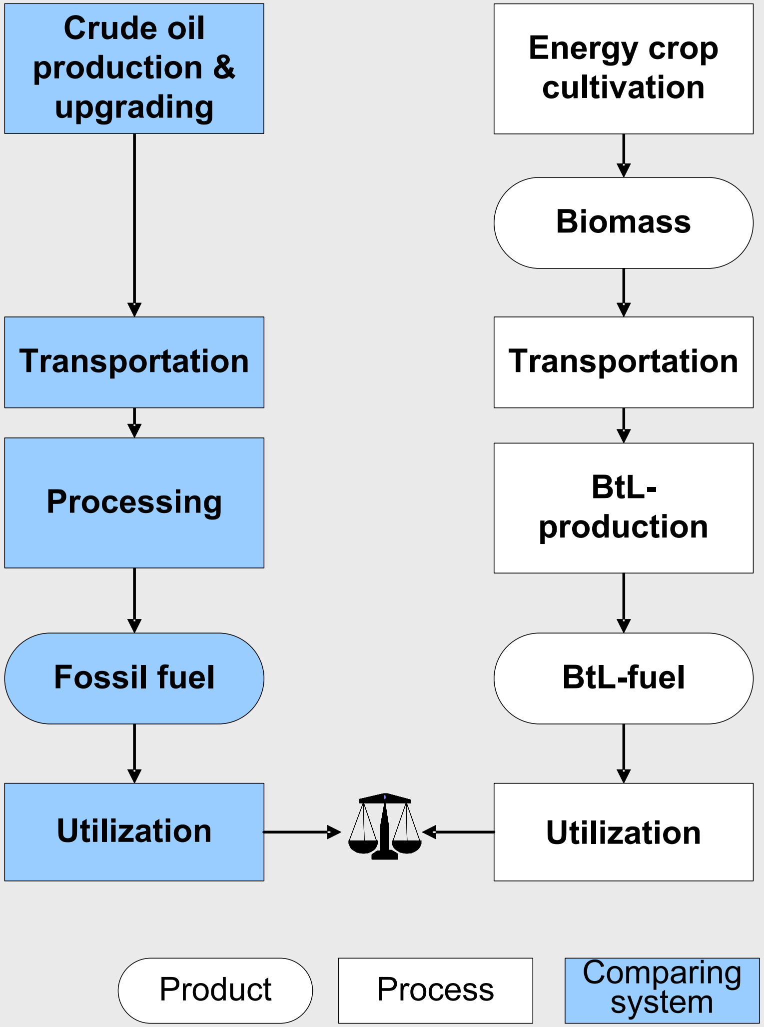
ct/kWh	MeOH	DME	MtG	FT	SNG	DMEdirect
FICFB	40,61	39,95	51,93	31,65	9,71	24,13
Carbo-V	15,50	15,16	20,31	17,89	16,15	18,71
H-DWS	20,93	21,41	25,24	22,32	12,95	12,82
S-DWS	20,21	20,36	24,22	21,73	12,38	12,27
H-bioliq	20,11	19,56	25,12	22,62	21,05	23,47
S-bioliq	16,68	16,34	21,04	19,16	17,66	13,35

- Composition of the production costs (routes with methanol as product)

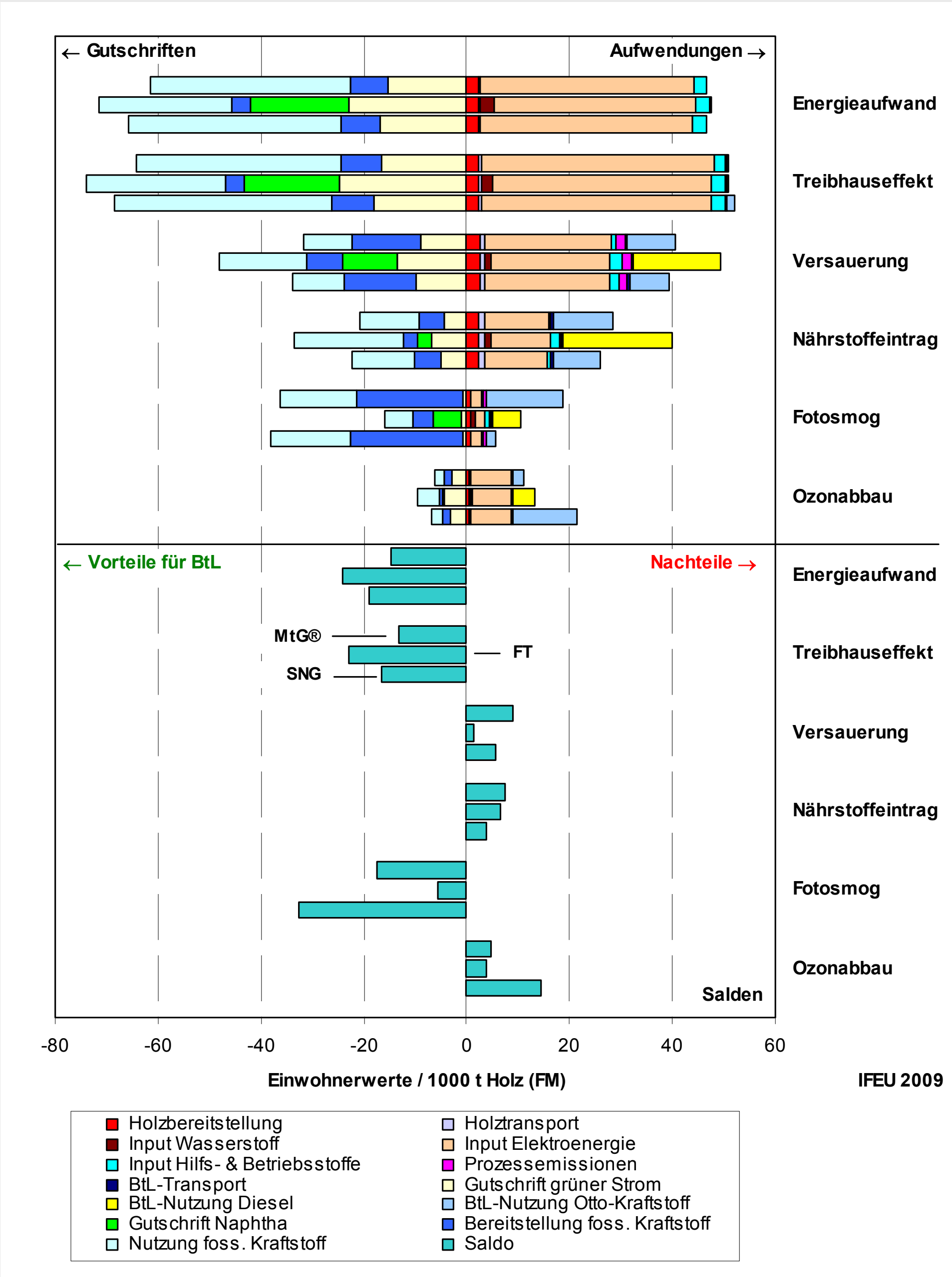


Example for Economic and Ecologic calculations

- Following ISO 14040 & 14044
- Overview balances with following elements:
  - In- and output streams (feedstock, materials, energy, waste water, waste, emissions)
  - Potential environmental impacts of the fuels
  - Whole life cycle: cultivation – gasification – synthesis – fuel utilization
- Investigated environmental impacts:
  - Energy demand
  - Greenhouse effect
  - Acidification
  - Eutrophication
  - Summer smog
  - Ozone depletion



Example for Economic and Ecologic calculations



Main results

- Advantages BtL:
  - Energy saving
  - Reduction of greenhouse effect
- Disadvantages:
  - Acidification
  - Eutrophication
- No general statement regarding environment-friendly gasification or synthesis process possible
- No general statement regarding global preferableness of BtL-fuels possible
- Individual verification necessary

Conclusion

- Several processes with different stages of development
- Only MTG and COD run successfully in commercial scale:
  - MTG: 1985 – 1995 in New Zealand, 3 new projects in China and USA,
  - COD: PetroSA (Mossgas) Refinery.
- Other processes only lab- or pilot-scale.
- German STF and bioliq® (Stage IV) project will demonstrate new technologies (or not).
- Selection of fuel syntheses depends on syngas composition.
- Comparison of different BTL-routes with uniform boundary conditions show wide array of results.
- Individual investigations necessary.
- High production costs.
- Feedstock supply infrastructure is bottleneck.