Fuel production from biomass-derived syngas within the bioliq®-process

IEA Bioenergy Agreement: 2007-2009
Task 33: Thermal Gasification of Biomass
First Semi-annual Task Meeting 2009
May 13-15, 2009, Karlsruhe, Germany

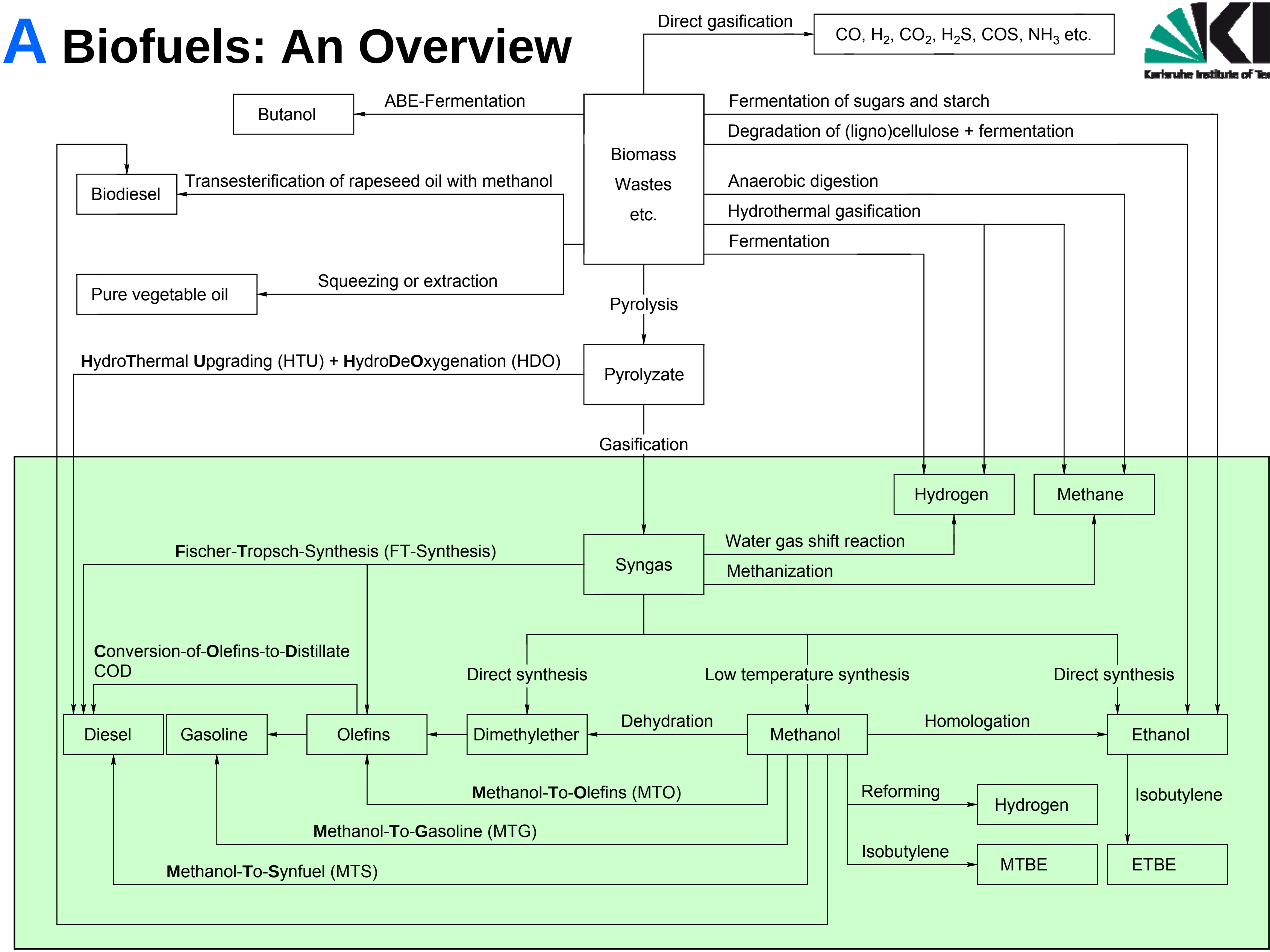
Ulrich Arnold, Manfred Döring, Nicolaus Dahmen, Eckhard Dinjus
Forschungszentrum Karlsruhe GmbH
ITC-CPV

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

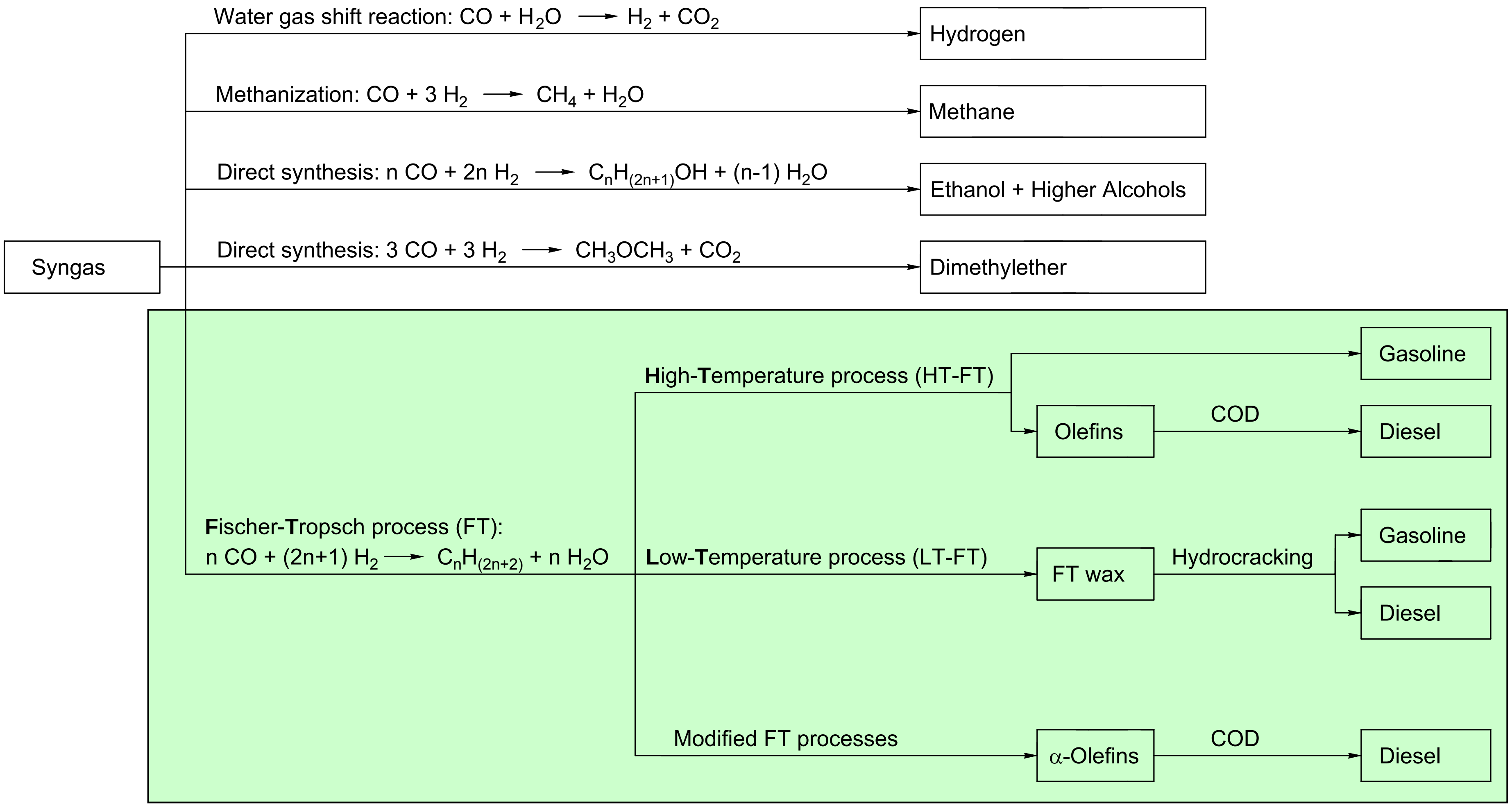
Universität Karlsruhe (TH)
Research University • founded 1825

Content

A Biofuels: An Overview

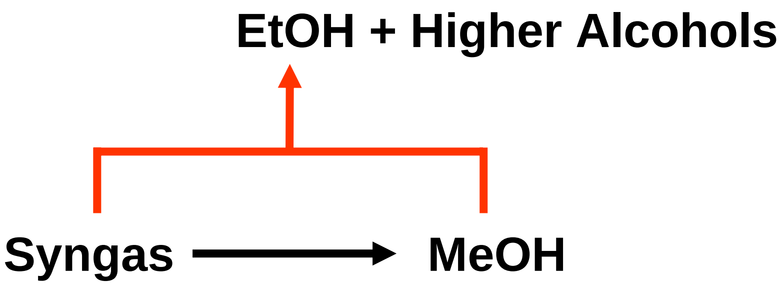


A1 Production of biofuels *via* syngas: "Non-methanolic pathways"



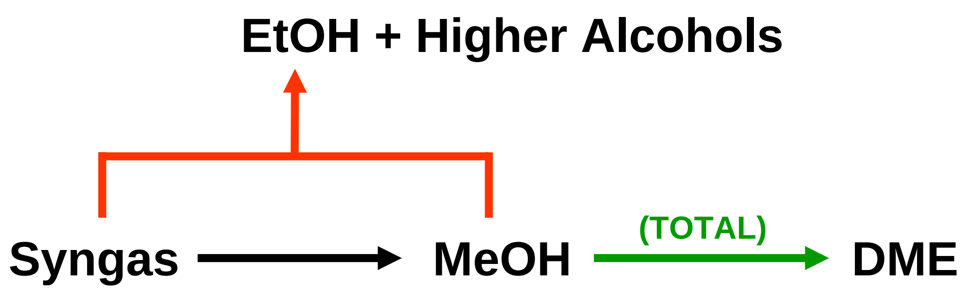
A2 Production of biofuels *via* methanol (MeOH):

Processes and some involved companies



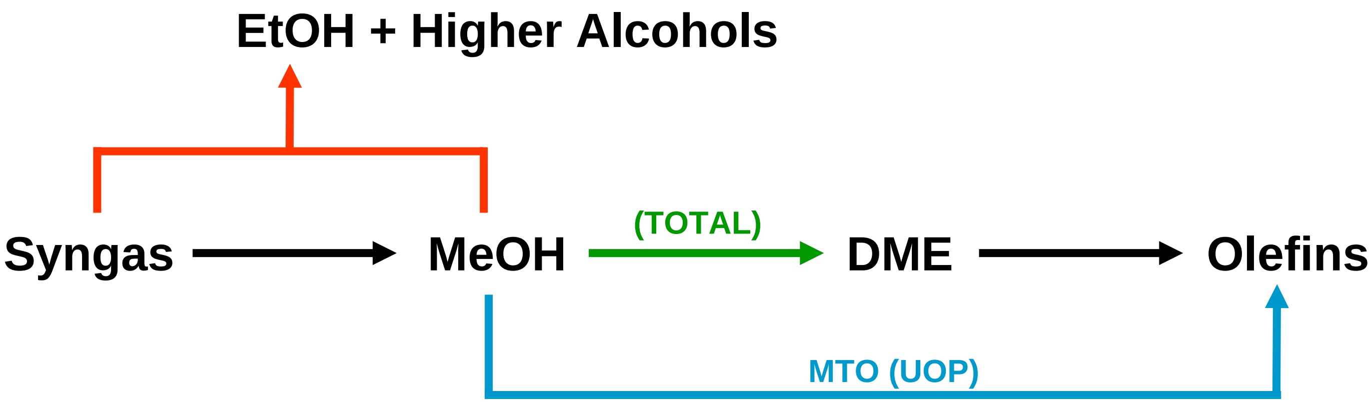
A2 Production of biofuels *via* methanol (MeOH):

Processes and some involved companies



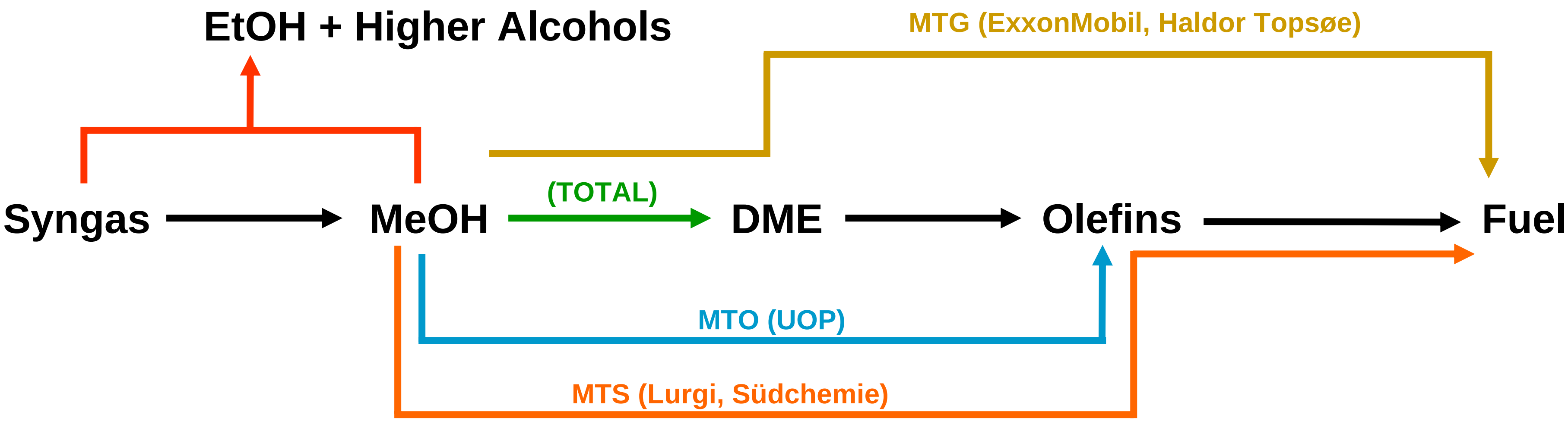
A2 Production of biofuels *via* methanol (MeOH):

Processes and some involved companies



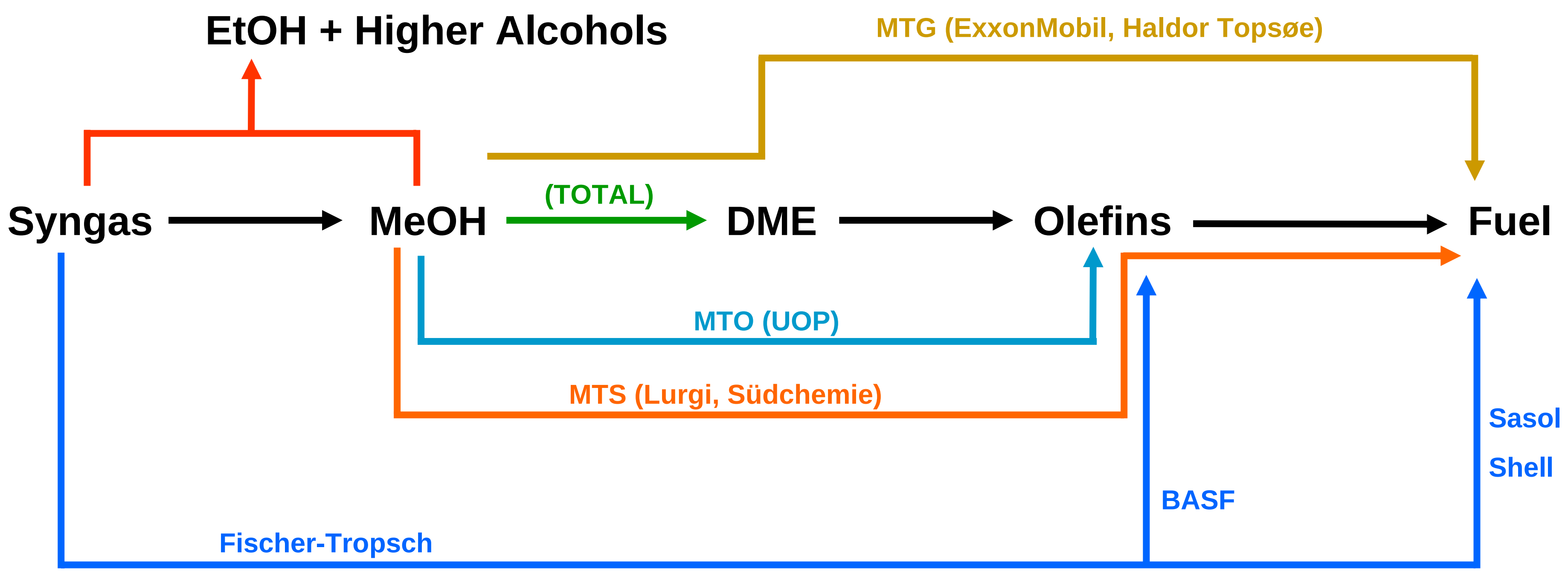
A2 Production of biofuels *via* methanol (MeOH):

Processes and some involved companies

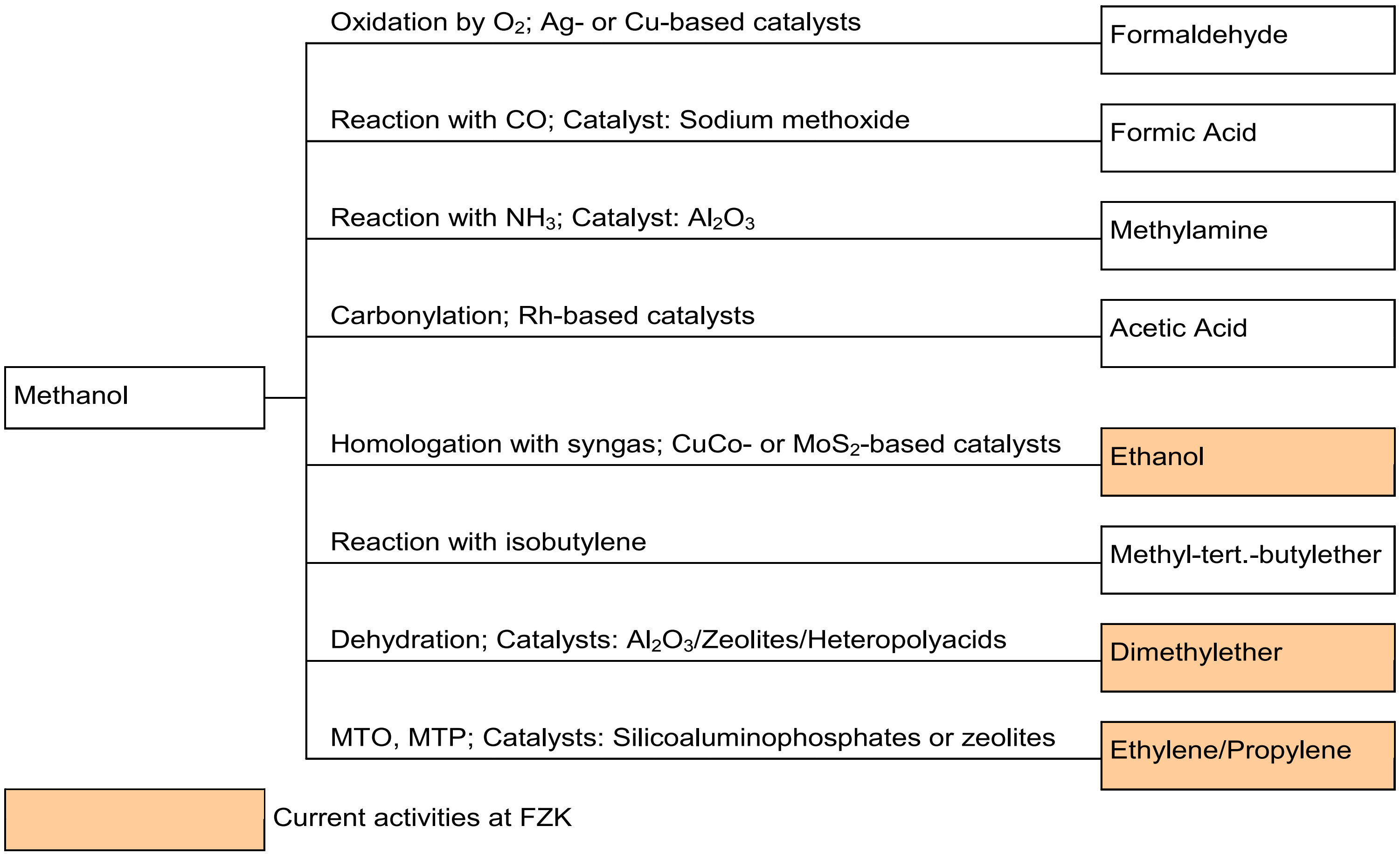


A2 Production of biofuels *via* methanol (MeOH):

Processes and some involved companies



A2 Production of chemicals from methanol



Direct formation from syngas is also desirable

B The bioliq®-process: Current status

Step	bioliq® I	bioliq® II	bioliq® III	bioliq® IV
Process	Fast Pyrolysis	Syngas Generation	Syngas Conditioning and Synthesis of MeOH/DME	Fuel Production
Technology	Twin Screw Reactor	Entrained Flow Gasification	Gas Cleaning: Rectisol Low Pressure Methanol Synthesis and/or Direct DME Synthesis	MTS or MTG*
Main product	bioliqSyncrude®	Syngas	Methanol and/or DME	Gasoline and/or Diesel
Status	Completed	Advanced Planning Stage	Planning Stage	Planning Stage
Involved	FZK, Lurgi	FZK, Lurgi		

*Methanol-To-Synfuel, Methanol-To-Gasoline

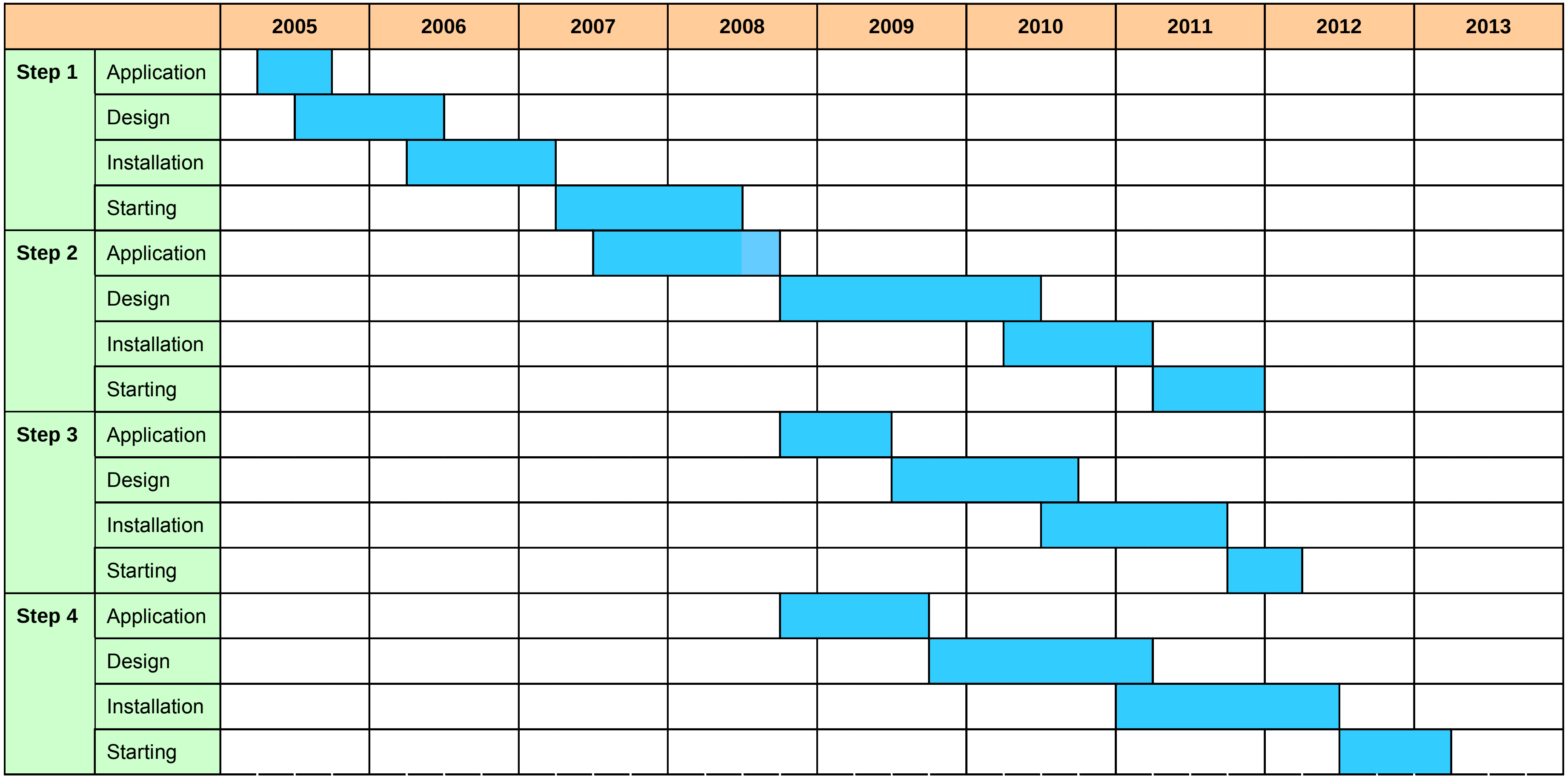
Sponsored by:

FACHAGENTUR NACHWACHSENDE ROHSTOFFE e.V.

Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz

In cooperation with: Lurgi

B The bioliq®-process: Timetable

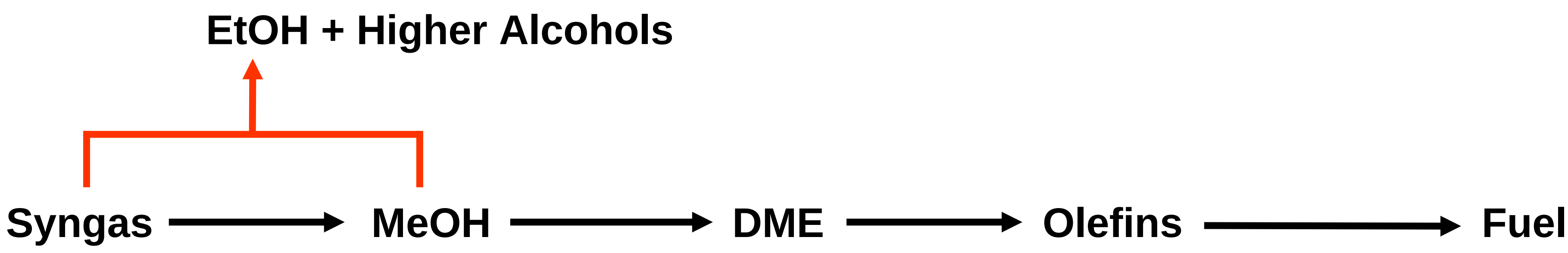


B The bioliq®-process: Technologies and scale

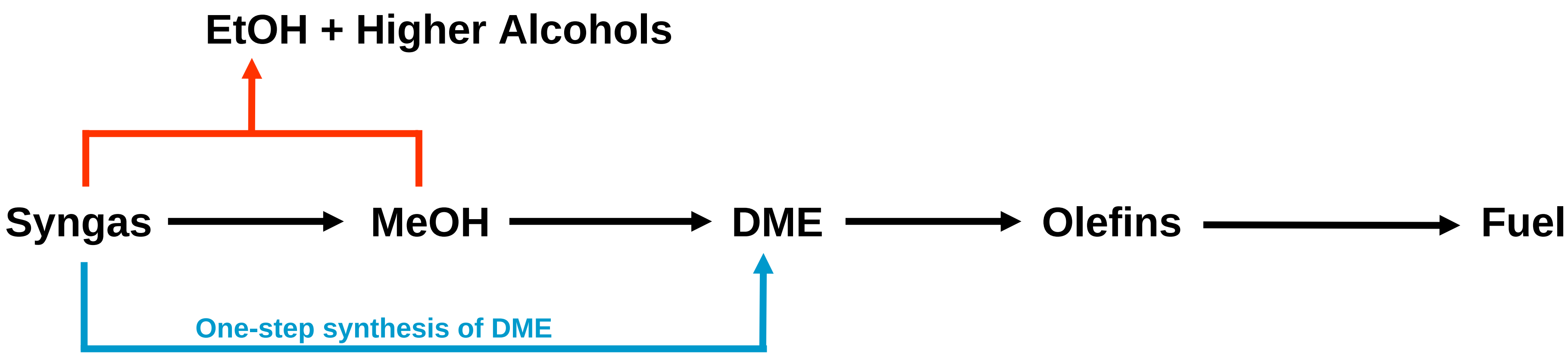
Step	Start Conditions	bioliq® I Biomass Pyrolysis	bioliq® II Syngas Generation	bioliq® III Syngas Conditioning and Synthesis of MeOH/DME		bioliq® IV Fuel Production	
				bioliq® IIIa Syngas Conditioning	bioliq® IIIb Synthesis of MeOH/DME		
Technology	–	Fast Pyrolysis	Entrained Flow Gasification	Rectisol + Sweet CO-Shift	Low Pressure Process	MTG[a]	MTS[b]
Dimensioning	–	2 MW	5 MW[c]	Max. 1000 Nm^3/h	5 MW	5 MW	5 MW
Volume Flow	2.44-7.69 m^3/t_{LCAD}[d,e]	0.59-0.68 m^3/t_{LCAD}	Max. 1000 Nm^3/h Syngas	Max. 1000 Nm^3/h Syngas	268 l/h Methanol	Max. 100 l/h Gasoline	Max. 100 l/h Fuel
Mass Flow	~ 500 kg/h Biomass	~ 333 kg/h bioliqSyncrude®	~ 490 kg/h Raw gas		~ 212 kg/h Methanol	~ 76-82 kg/h Gasoline	~ 86 kg/h Fuel
Percentage Energy Content	~ 100%	~ 88%	~ 70%		~ 60%	~ 45%	~ 45%

[a]MTG = **M**ethanol-**T**o-**G**asoline; [b]MTS = **M**ethanol-**T**o-**S**ynfuel; [c]Security aspects and scale-up options; [d]E. Henrich, N. Dahmen, E. Dinjus, *Biofuels, Bioprod. Bioref.* **2009**, *3*, 28-41; [e]LCAD = Ligno-cellulose (air-dry)

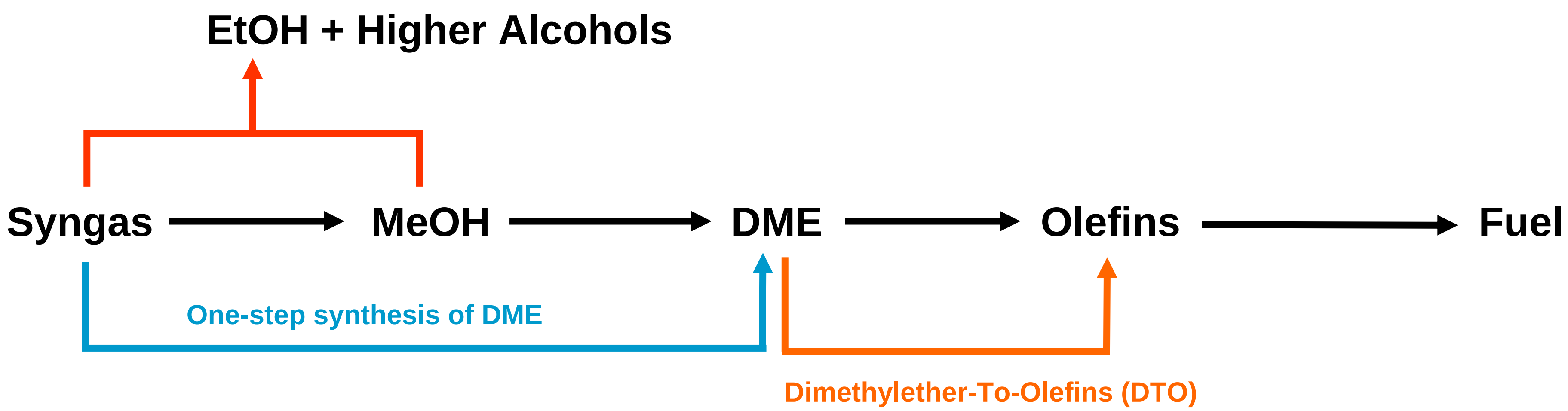
C Fuel-production within the bioliq®-process: Activities at Karlsruhe Research Center



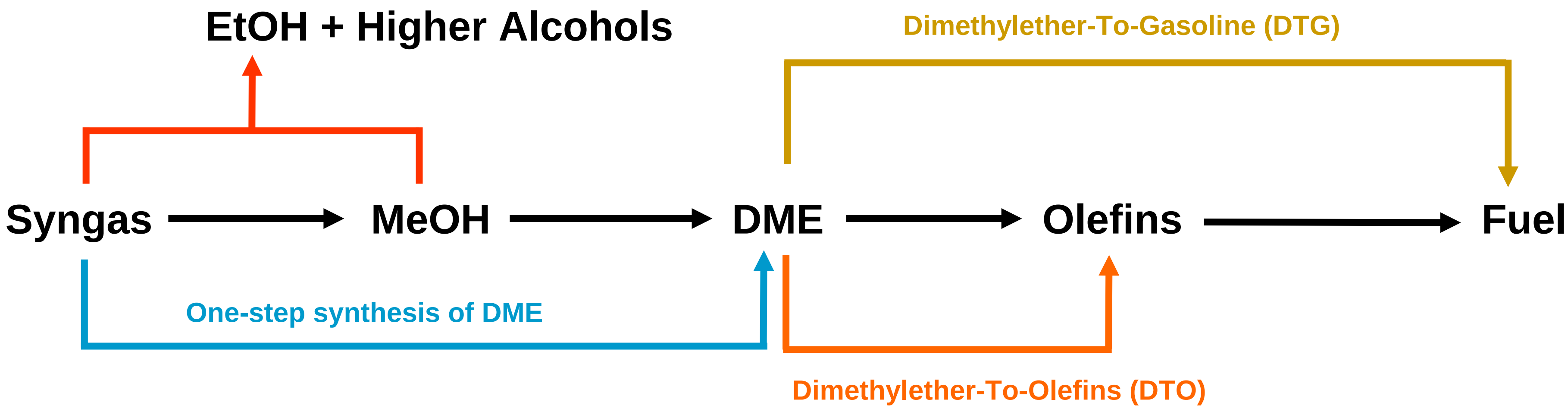
C Fuel-production within the bioliq®-process: Activities at Karlsruhe Research Center



C Fuel-production within the bioliq®-process: Activities at Karlsruhe Research Center



C Fuel-production within the bioliq®-process: Activities at Karlsruhe Research Center



- Synthesis of ethanol and higher alcohols from syngas:
  $n\ CO + 2n\ H_2 \rightarrow C_nH_{(2n+1)}OH + (n-1)\ H_2O$
- Synthesis of ethanol and higher alcohols from methanol + syngas:
  $CH_3OH + n\ CO + 2n\ H_2 \rightarrow C_{(n+1)}H_{(2n+3)}OH + n\ H_2O$

C1 Fuel-production within the bioliq®-process: Production of Methanol (MeOH)

Methanol synthesis

$CO + 2\,H_2 \rightleftharpoons CH_3OH$ $\Delta H = -91$ kJ/mol

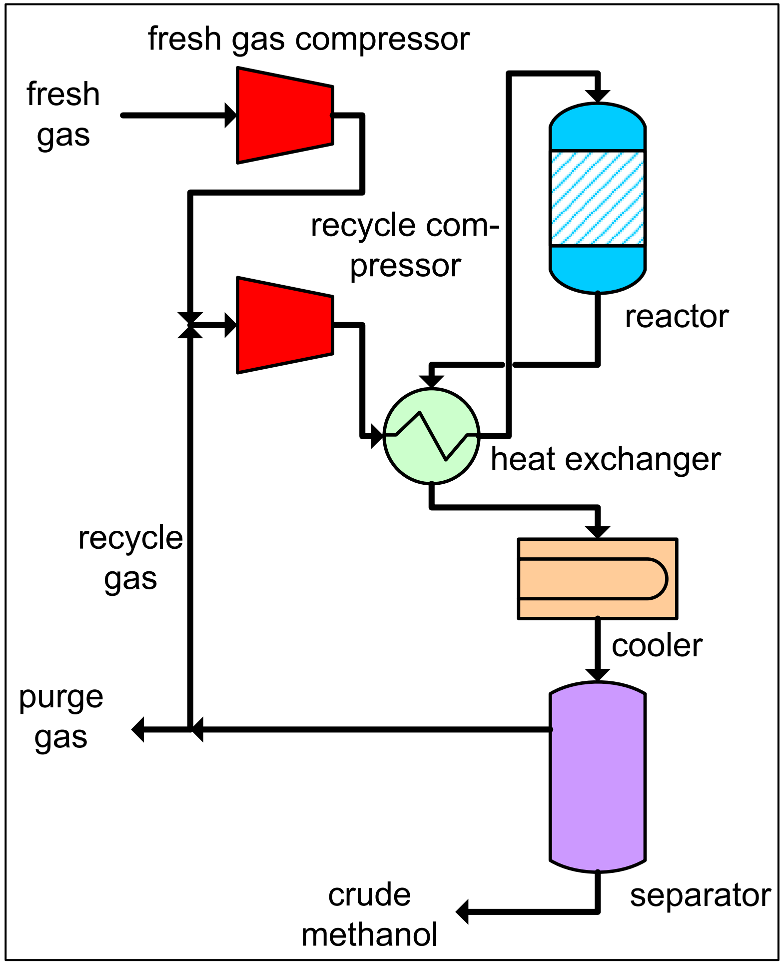
Side reactions

$CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\Delta H = +41$ kJ/mol

$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta H = -49$ kJ/mol

Scale and conditions

- ~ 200 l/h MeOH
- 50 -100 bar
- 250 °C
- Cu-ZnO-Al_2O_3 catalyst



C2 Fuel-production within the bioliq®-process: Production of Dimethylether (DME)

DME synthesis

$2\,CO + 4\,H_2 \rightleftharpoons 2\,CH_3OH$	$\Delta H = -182$ kJ/mol
$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$	$\Delta H = -24$ kJ/mol
$2\,CO + 4\,H_2 \rightleftharpoons CH_3OCH_3 + H_2O$	$\Delta H = -206$ kJ/mol

- If the water gas shift reaction is supported by the catalyst:

$CO + H_2O \rightleftharpoons CO_2 + H_2$	$\Delta H = -41$ kJ/mol
$3\,CO + 3\,H_2 \rightleftharpoons CH_3OCH_3 + CO_2$	$\Delta H = -247$ kJ/mol

- Favorable in the case of CO-rich gases

Three major markets

- **Power generation**
  Fuel for gas turbines in medium sized power plants (Mitsubishi, Hitachi, GE)
- **Domestic LPG Substitute**
  DME can be blended in up to 20% in LPG
- **Automotive Fuel**
  "Diesel LPG" with high cetane number

C2 Fuel-production within the bioliq®-process: Dimethylether as a LPG substitute

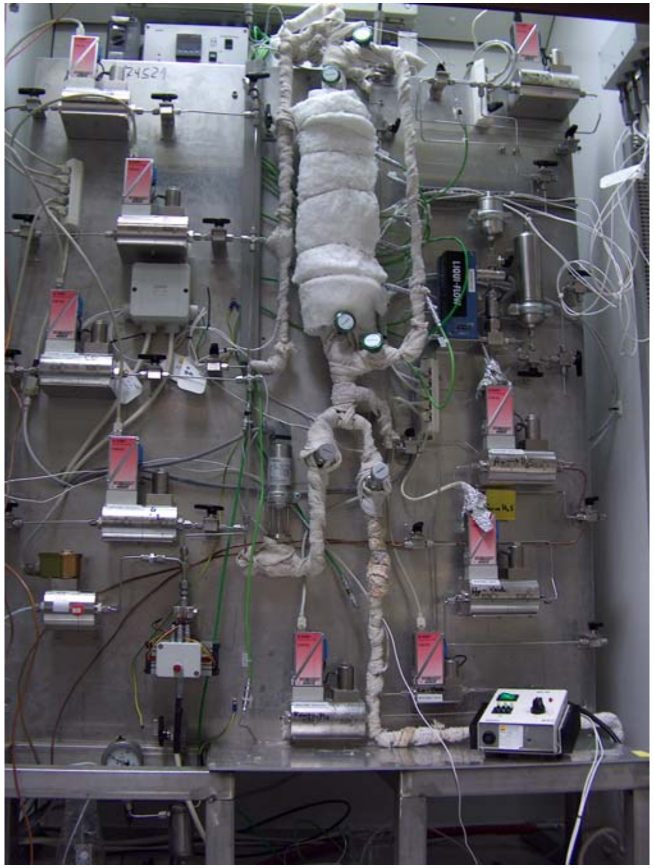
Properties of DME compared to liquid gases

	DME	Propane	Butane
Boiling Point (°C)	–24.9	–42.1	–0.5
Vapour Pressure at 20 °C (bar)	5.1	8.4	2.1
Specific Density at 20 °C (kg/m^3)	1.59	1.52	2.01
Lower Heating Value (MJ/kg)	28.43	46.36	45.74
Auto Ignition at 1 atm (°C)	235-350	470	365
Expl.-Flamm. Limit in Air (Vol%)	3.4-17	2.1-9.4	1.9-8.4
Cetane number	55 to 60	5	10

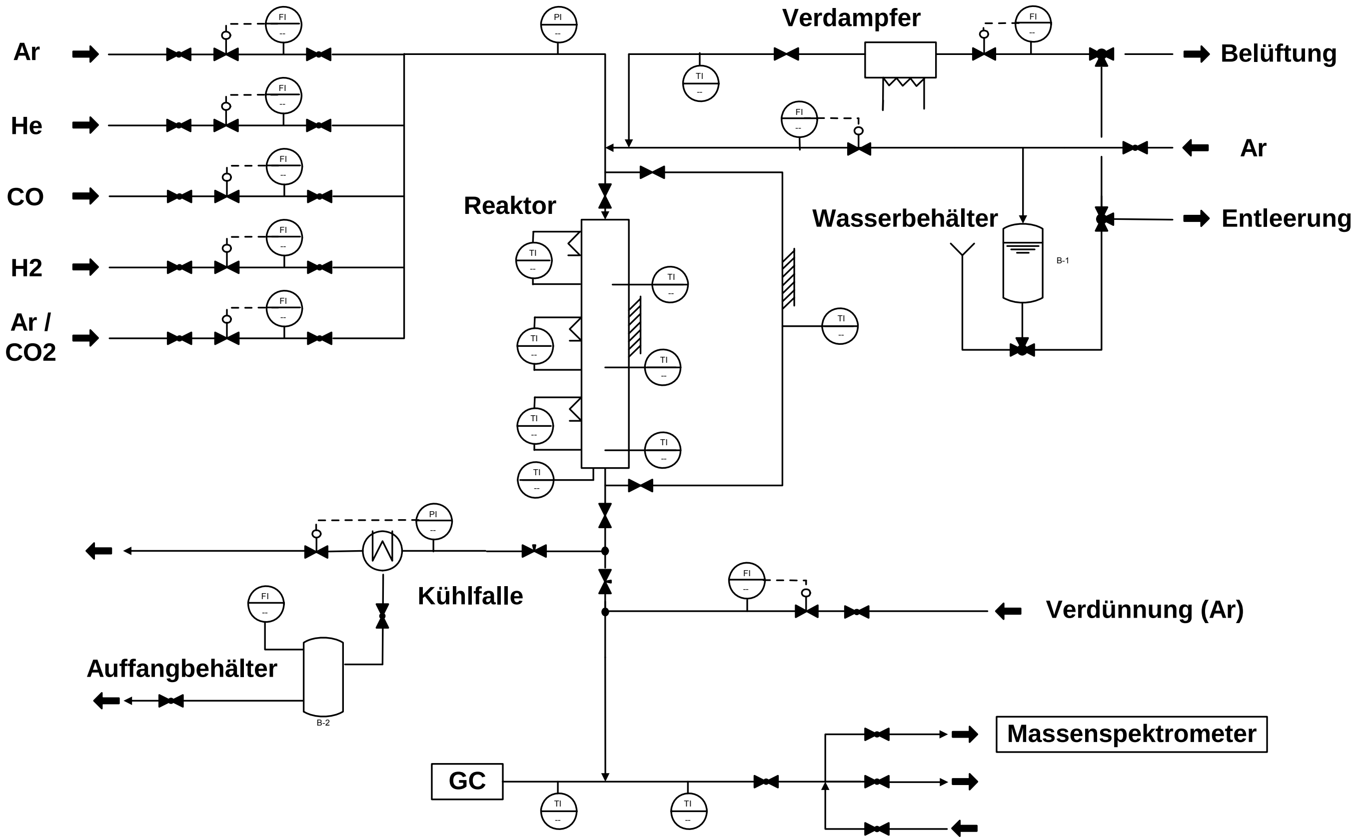
C2 Fuel-production within the bioliq®-process: Production of Dimethylether (DME)

Preliminary work at ITC-CPV:

- Development of a one-step synthesis combining methanol formation from syngas and methanol dehydration
- Optimization of (poisoning-resistant) catalysts and reaction parameters
- Optimization of conversions and selectivities
- Development of a continuously operating process set-up and investigations under long-term operating conditions
- Study of reaction mechanisms and kinetics
- Installation of a laboratory plant



C2 Fuel-production within the bioliq®-process: One-step synthesis of dimethylether (DME) from syngas in a laboratory plant



Fixed bed reactor:

- Diameter: 16 mm
- Length: 300 mm
- Volume: 60.3 ml

C2 Fuel-production within the bioliq®-process: One-step synthesis of dimethylether (DME) from syngas

Syngas	τ [s]	T [°C]	C_{CO} [%]	S_{DME} [%]	S_{CO2} [%]	S_{MeOH} [%]
$H_2/CO = 2$	40,1	200	16,0	67,4	31,1	1,6
	36,3	250	68,9	67,4	31,3	1,3
	72,5	200	35,3	67,3	31,1	1,5
	80,2	250	73,3	66,6	32,2	1,2
$H_2/CO = 1$	40,1	200	9,2	67,3	31,9	0,8
	36,3	250	49,1	66,5	32,8	0,8
	72,5	200	20,8	67,3	31,9	0,8
	80,2	250	57,3	66,4	32,9	0,7
$H_2/CO = 0.67$	40,1	200	5,4	66,8	32,5	0,6
	36,3	250	34,2	66,0	33,3	0,6
	72,5	200	14,9	67,0	32,5	0,6
	80,2	250	41,9	65,9	33,5	0,6

Reaction conditions:

- Pressure: 51 bar
- Temperature: 200 - 250 °C
- Space velocity: 20 - 150 Nml/(min·g_{Cat})
- Dilution: 70% Ar

C2 Fuel-production within the bioliq®-process: One-step synthesis of dimethylether (DME) from syngas

- High H_2-content promotes CO-conversion
- High DME-selectivity also at H_2/CO-ratios ≤ 1
- Large influence of temperature and contact time on CO-conversion
- Main byproduct: CO_2 ⇒ Water-gas-shift-reaction is catalyzed
- Low MeOH-concentrations ⇒ Fast dehydration
- Byproducts: Propylene, butylene, methane on a very low level

C3 Production of olefins *via* Methanol-To-Olefin (MTO) processes

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H = -24\ kJ/mol$$
$$CH_3OCH_3 \rightarrow (CH_2)_2 + H_2O \qquad \Delta H = -19\ kJ/mol$$

UOP/Norsk-Hydro: UOP/HYDRO MTO Process
Catalyst: Silicoaluminophosphat SAPO-34

UOP/HYDRO MTO Process: Propylene/Ethylene Ratios

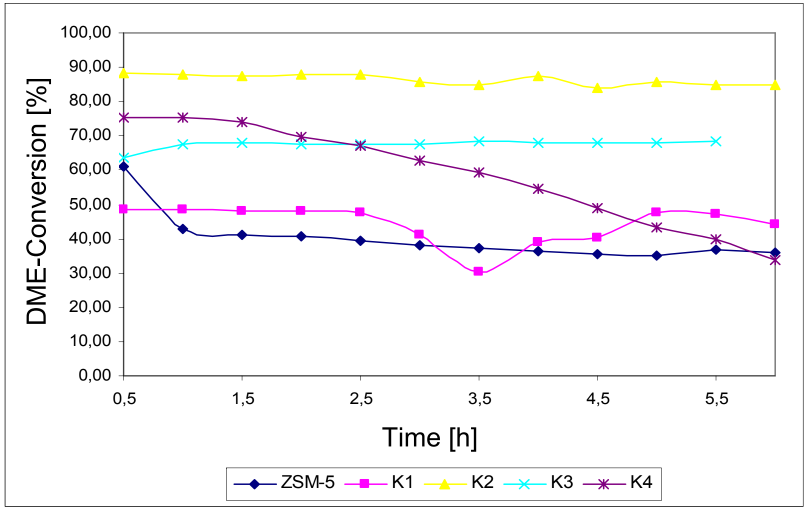
Products (Wt. Ratios)	High Ethylene Mode	High Propylene Mode
Ethylene	0.57	0.43
Propylene	0.43	0.57
Butenes & Heavier	0.19	0.28
C3=/C2=	0.77	1.33

- Further suppliers of MTO technologies: Lurgi, Japan DME Ltd. etc.
- The olefins can be converted in a following *Conversion of Olefins to Distillate* (COD) step to high quality fuels

C4 Production of olefins *via* MTO and DTO processes (Dimethylether-To-Olefin)

Preliminary work at ITC-CPV:

- Preparation and modification of SAPO catalysts to improve MTO activity
- Development of a selective Dimethylether-To-Olefin (DTO) process



Selectivities: ~30% propylene, ~10% ethylene, + higher hydrocarbons

Reaction conditions:

- Pressure: 1 bar
- Temperature: 450 °C
- Space velocity: 80 Nml/(min·g_{Cat})
- Dilution: 80% Ar

C5 Production of fuels *via* Methanol-To-Gasoline (MTG) processes

Simplified chemistry of the MTG-process:

$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$

$n\ CH_3OCH_3 + n\ CH_3OH \rightarrow$ “$(CH_2)_{3n}$“ $+ 2n\ H_2O$

$n\ CH_3OCH_3 \rightarrow$ “$(CH_2)_{2n}$“ $+ n\ H_2O$

ExxonMobil MTG process: Products from 1000 t of methanol

Product	Amount (t)
Gasoline	387
Liquefied Petroleum Gas (LPG)	46
Fuel gas	7
Water	560

- Catalyst: Zeolitic ZSM 5-type
- Further suppliers: E.g. Haldor Topsøe A/S (TIGAS Process)
- Development of a Dimethylether-To-Gasoline (DTG) process at FZK

C5 Production of fuels *via* Methanol-To-Gasoline (MTG) processes

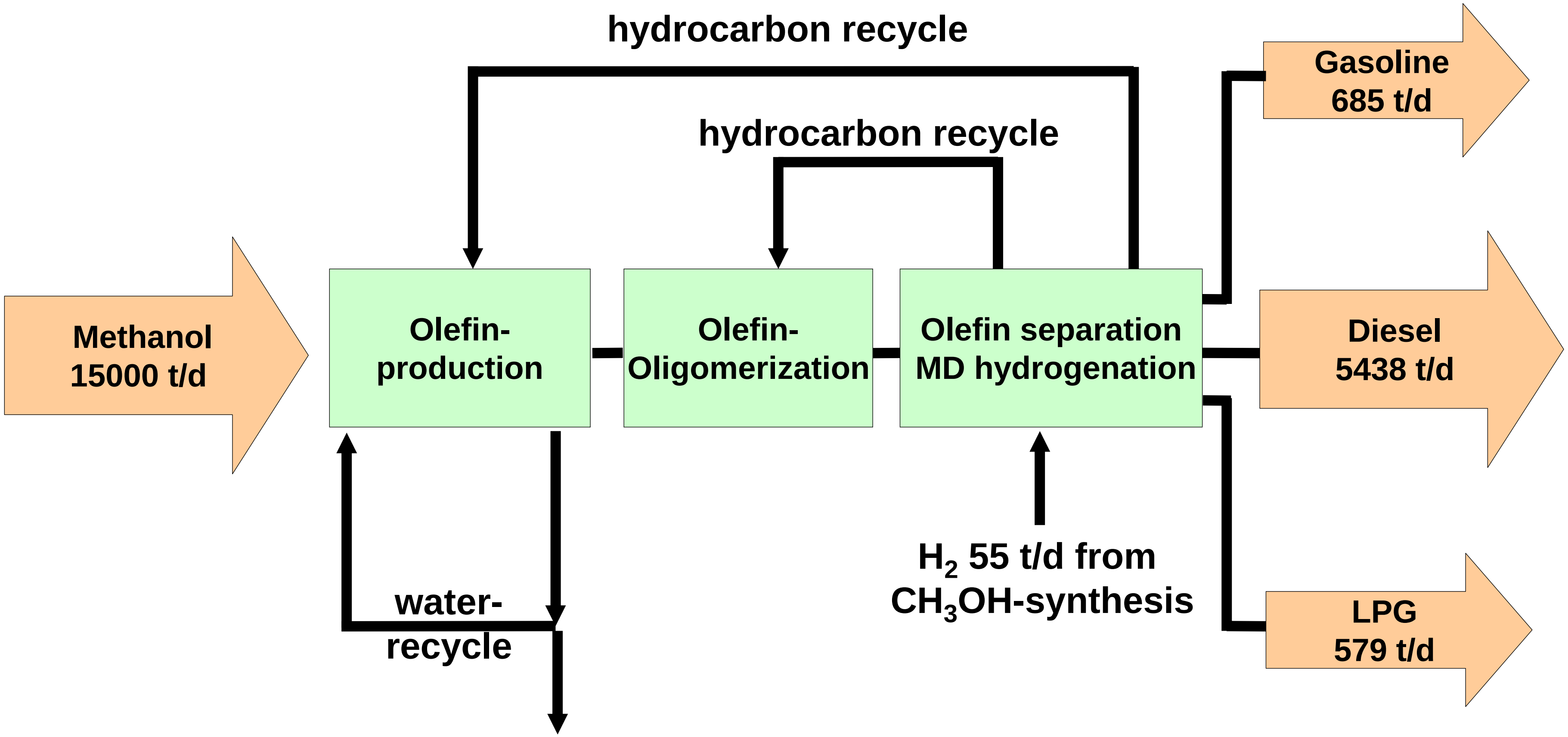
2007 DKRW Advanced Fuels
+ ExxonMobil Research and Engineering Company (EMRE)
Medicine Bow, WY, USA
Coal to Liquids (CTL) project based on Exxon Mobil Technology: 15000 bpd

2006 JAM (Shanxi Jincheng Anthracite Coal Mining Co. Ltd.) + Uhde
(Uhde license from EMRE)
Jincheng, Shanxi Province, China
CTL: 100000 t/a of gasoline from the year 2008

1985 Mobil + New Zealand Government
Montunui, New Zealand
MTG: 14500 bpd

1982 Mobil + Uhde
UK Wesseling, Germany
Refinery of Union Rheinische Braunkohlenkraftstoff AG: 25 t/d

C6 Production of fuels *via* Lurgi's Methanol-To-Synfuels (*MtSynfuels*) process



Source: W. Liebner, M. Wagner, *Erdöl, Erdgas, Kohle* **2004**, *10*, 323–326.
W. Balthasar, W. Hilsebein, *Nitrogen & Methanol* **2003**, *261*, 41-49.

C6 Production of fuels *via* Lurgi's Methanol-To-Synfuels (*MtSynfuels*) process

Lurgi's *MtSynfuels* process:

- Similar to the **M**obil **O**lefin to **G**asoline/**D**istillate (MOGD) process
- Gasoline (RON 80)/Diesel(Cetane ~55) of approximately 1:4
- With respect to product spectrum: More comparable to FT than to MTG
- But: Higher product flexibility compared to FT process

C7 Production of fuels *via* Fischer-Tropsch processes

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{(2n+2)} + n\,H_2O \qquad \Delta H = -165\ kJ/mol$$

1993 Shell: Bintulu, Malaysia
Middle **D**istillate **S**ynthesis (MDS) Process
Capacity of ca. 500000 t/a

1955- Sasol: South Africa
Total capacity of 5.4 Mio t/a

1944 Germany, 9 plants with a total capacity of 600000 t/a

1925 Discovery by
Franz Fischer & Hans Tropsch

Potential Fischer-Tropsch licensors

Licensor	Commercial References	Reactor system	Catalyst
SASOL	yes	fixed bed/slurry phase fluidized bed	iron/cobalt
SHELL	yes	fixed bed	cobalt
CONOCO PHILLIPS	no	slurry phase	cobalt
RENTECH	no	slurry phase	iron
SYNTROLEUM	no	fixed bed	cobalt
BP	no	fixed bed	cobalt
STATOIL	no	slurry phase	cobalt
EXXON MOBIL	no	slurry phase	cobalt
ENI	no	slurry phase	cobalt

Catalysts: Iron and cobalt catalyst systems

Iron catalysts:
- Cheaper than cobalt catalysts
- More flexible and robust
- Syngas H_2:CO ratios of 0.7:1 up to 2:1

Cobalt catalysts:
- H_2:CO ratio of 2:1
- Longer lifetime than iron catalysts
- Higher selectivity than iron catalysts

C7 Selective production of α-olefins in modified Fischer-Tropsch processes

Control of product distribution, essentially by

- **Choice of catalyst**

  e.g. Fe-, Fe+Co-, FeCo-Spinel-, CoMn-Spinel- or Cu-doped Co-catalysts

- **Choice of reaction conditions**

  Temperature, pressure, syngas composition, feeding of α-olefins into the reaction zone etc.

- **Choice of process and reactor type**

  e.g. Combination of Fischer-Tropsch process with distillation process (BASF DE 10 2005 056 784)

BASF:
- Product containing at least 50 wt.% of olefins
- Particularly α-olefins
- High Selectivity to C_4-C_{14}=

C7 Why the methanol pathway instead of a Fischer-Tropsch process?

- High flexibility: Production of various fuels and chemicals is possible
- High selectivity: No elaborate product separation technologies
- Processes are tunable to a large extent (catalysts, conditions, reactors etc.)
- Large optimization potential based on established technologies

Comparison of Fischer-Tropsch with MTG

Compound	LT-FT Co Catalyst 220 °C	HT-FT Fe Catalyst 340 °C	MTG
Methane	5	8	0.7
Ethylene	0	4	–
Ethane	1	3	0.4
Propylene	2	11	0.2
Propane	1	2	4.3
Butylenes	2	9	1.1
Butane	1	1	10.9
C5+ Gasoline	19	36	82.3
Gasoil/Distillate	22	16	–
Heavy Oil/Wax	46	5	–
Oxygenates	1	5	0.1
Σ	100	100	100

Source:

- http://nzic.org.nz/ChemProcesses/energy
- *Fischer-Tropsch Technology*, (Ed.s: A. Steynberg, M. Dry), Elsevier, Amsterdam, **2004.**

B The bioliq®-process: Technologies and scale

Step	Start Conditions	bioliq® I Biomass Pyrolysis	bioliq® II Syngas Generation	bioliq® III Syngas Conditioning and Synthesis of MeOH/DME				bioliq® IV Fuel Production	
				bioliq® IIIa Syngas Conditioning			bioliq® IIIb Synthesis of MeOH/DME		
Technology	–	Fast Pyrolysis	Entrained Flow Gasification	H_2S-Rectisol	CO-Shift	CO_2-Rectisol	Low Pressure Process	MTG[a]	MTS[b]
Dimensioning	–	2 MW	5 MW[c]	Max. 1000 Nm³/h Syngas	Max. 1000 Nm³/h Syngas	Max. 1000 Nm³/h Syngas	2/5 MW	2/5 MW	2/5 MW
Mass Flow	500 kg/h Biomass	333 kg/h bioliqSyncrude®	490 kg/h Raw gas			212 kg/h Syngas	212 kg/h (6.625 kmol) Methanol	76-82 kg/h Gasoline	86 kg/h Fuel
Volume Flow	2.44-7.69 m^3/t_{LCAD}[d,e]	0.59-0.68 m^3/t_{LCAD}	Max. 1000 Nm³/h Syngas	Max. 1000 Nm³/h Syngas	Max. 1000 Nm³/h Syngas	Max. 1000 Nm³/h Syngas	268 l/h Methanol	Max. 100 l/h Gasoline	Max. 100 l/h Gasoline
Percentage Energy Content	100% (2.2 GJ/m³)	88% (22 GJ/m³)				72%	61%	45%	~ 45%
Conditions	LCAD = Air-dry Lignocellulose	1200 °C ≥ 60 bar + O_2 τ = 2-3 s	79.522 kmol/h 38 bar, 45 °C H_2: 24.53 kmol/h CO: 28.28 kmol/h CO_2: 14.88 kmol/h N_2: 11.51 kmol/h ~ 1800 Nm³/h 80 or 40 bar H_2: 27 Vol.% CO: 50 Vol.% CO_2: 14 Vol.% N_2: 6 Vol.%	Alternative: *Absorption* Purisol Selexol Sepasolv Fluor-Solvent Amine-, Alkalicarbonate-, Base-, NH_3-Cleaning Sulfinol Amisol Sulfosolvan *Adsorption*	Sweet CO-Shift HTS: Fe_2O_3-Cr_2O_3 300-510 °C and/or LTS: Cu-ZnO-Al_2O_3 180-270 °C Sour CO-Shift RGS: CoO-MoO_3-Al_2O_3 200-500 °C Sulfur-Activation	Alternative: Dry Gas Cleaning 80 bar, 350 °C CO/H_2 ≈ 1:1 Development at FZK	50-100 bar, 250 °C Cu-ZnO-Al_2O_3 Catalyst	*Mobil process* Fixed Bed DME-reactor 300-320 °C Conversion reactor: 400-420 °C Methanol: 1000 t Gasoline: 387 t LPG: 46 t Fuel gas: 7 t Water: 560 t ZSM-5 catalyst	*Lurgi process* MTO[f] MTP[g] COD[h] Methanol: 1000 t Diesel: 362 t Gasoline: 46 t Light oil: 39 t Water: 568 t

[a]MTG = Methanol-To-Gasoline; [b]MTS = Methanol-To-Synfuel; [c]Security aspects and Scale-up options; [d]E. Henrich, N. Dahmen, E. Dinjus, *Biofuels, Bioprod. Bioref.* **2009**, *3*, 28-41; [e]LCAD = Lignocellulose (air-dry); [f]MTO = Methanol-To-Olefins; [g]MTP = Methanol-To-Propylene; [h]COD = Conversion-of-Olefins-to-Distillate