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GREEN DIESEL FROM BIOMASS BY FISCHER-TROPSCH SYNTHESIS: NEW INSIGHTS IN GAS CLEANING AND PROCESS DESIGN

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Revisions		
A		
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Green Diesel from Biomass by Fischer-Tropsch Synthesis:

New Insights in Gas Cleaning and Process Design

PGBW Expert Meeting, 1 October 2002

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Hans-Peter Calis, Shell Global Solutions Int.

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Purpose & Content

Purpose: first-order and qualitative discussion
to obtain new insights

- Renewable transportation fuels
- Biomass gasification & Fischer-Tropsch synthesis
- Evaluated system & Design approaches
- Experimental demonstration
- Conclusions

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Renewable fuels

motivation for BG-FT

- Biomass-based fuels
  - reduction of CO_2 emissions (objectives Kyoto protocol)
  - important renewable energy source
- Directives from European Commission
  - 2% share in 2005 (for bio-fuels) to 6% in 2010
- Biomass gasification & Fischer-Tropsch synthesis
  = one of most promising routes *(GAVE study)*

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Definitions

for renewable fuels

Bio-diesel	liquid product from esterfication of vegetable oils (*e.g.* rapeseed oil = RME)
versus	
Green diesel	high-quality ultra-clean diesel-like product from Fischer-Tropsch synthesis
Biosyngas	gas rich in H_2 and CO obtained by gasification of biomass
Syngas	comparable to biosyngas, but from fossil origin
Bio-gas	from digestion of organic matter, consisting mainly of CH_4 and CO_2

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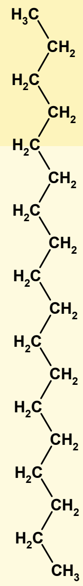
Fischer-Tropsch Synthesis

chemistry



- Synthesis of long-chain hydrocarbons from CO en H_2
- Catalytic reaction: $CO + 2\ H_2 \rightarrow -CH_2- + H_2O$
- Cobalt (Co) catalyst: superior activity and selectivity
- Exothermic reaction: 20% of energy released as heat
- Ratio H_2/CO adjustment by water-gas-shift:
  $CO + H_2O \leftrightarrow CO_2 + H_2$

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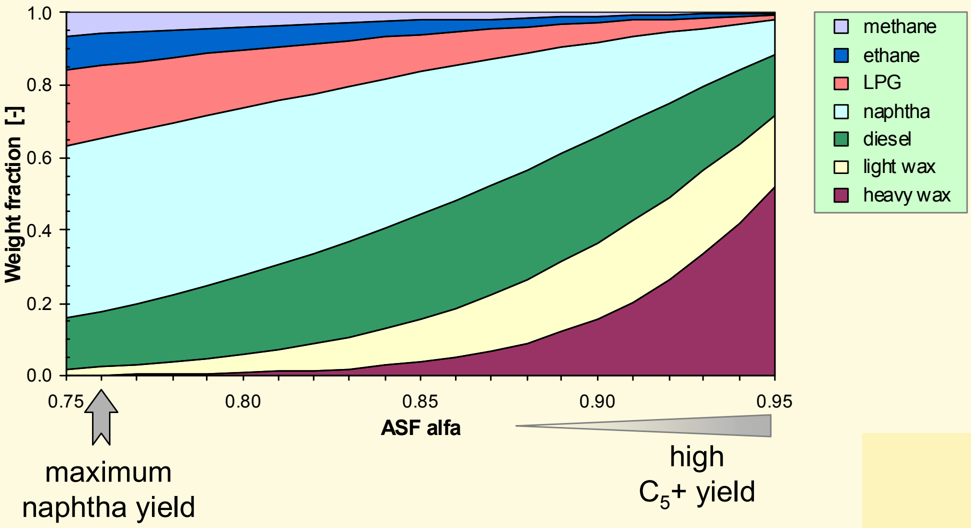
Products from FT Synthesis

Anderson-Schulz-Flory (ASF) relation



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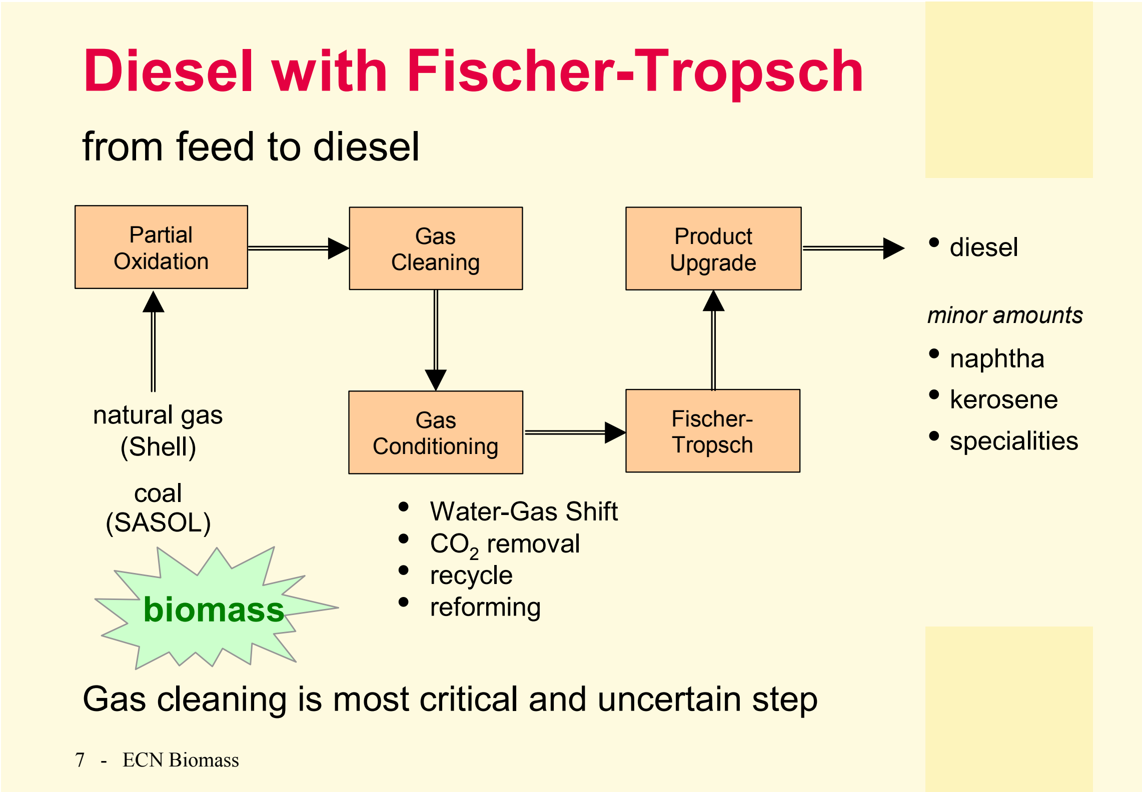
Diesel with Fischer-Tropsch
from feed to diesel
Partial Oxidation
Gas Cleaning
Product Upgrade
Gas Conditioning
Fischer-Tropsch
natural gas (Shell)
coal (SASOL)
biomass
• diesel
minor amounts
• naphtha
• kerosene
• specialities
• Water-Gas Shift
• CO_2 removal
• recycle
• reforming
Gas cleaning is most critical and uncertain step
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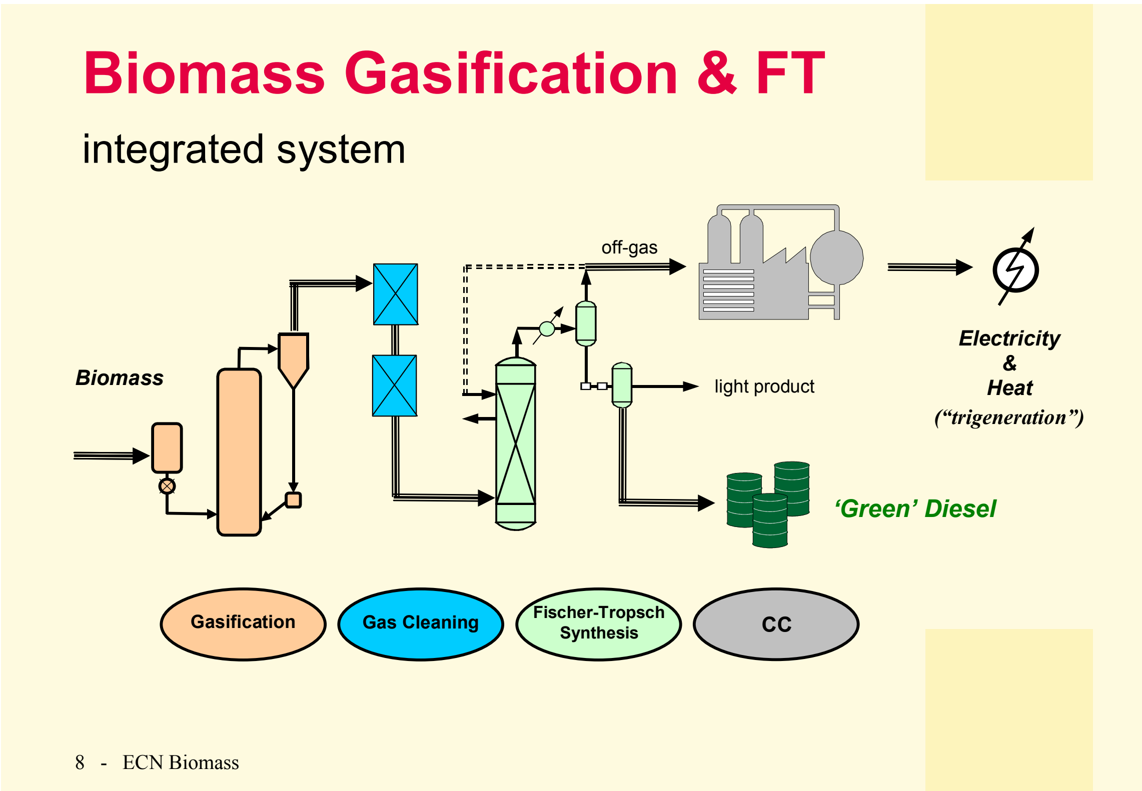
Biomass Gasification & FT
integrated system
Biomass
off-gas
light product
Electricity & Heat
(“trigeneration”)
‘Green’ Diesel
Gasification
Gas Cleaning
Fischer-Tropsch Synthesis
CC
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Evaluated System

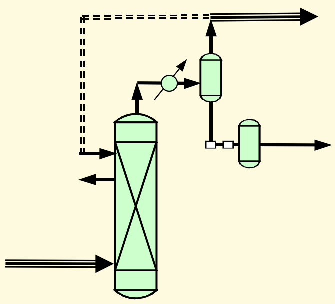
assumptions and choices

- Integrated BG-FT system, focus on gas cleaning
- Circulating Fluidised Bed (CFB) gasifier
  - *robust, scaleable, fuel-flexible, widely used*
  - *state-of-the-art = air-blown, atmospheric CFB*
- FT synthesis treated as black-box
  - *no optimisation and no product upgrading*
- Goal is to maximise production of FT liquids
- <u>Technical assessment !!!</u>

Fischer-Tropsch synthesis

specifications feed gas

Impurity	Removal level
$H_2S + COS + CS_2$	< 1 ppmV
NH_3 + HCN	< 1 ppmV
HCl + HBr + HF	< 10 ppbV
alkaline metals	< 10 ppbV
solids (soot, dust, ash)	essentially completely
organic compounds (tars)	below dew point
- class 2 (hetero atoms)	*< 1 ppmV*



- class 2 tars: phenol, pyridine, thiophene
- organic compounds also include BTX

Biomass Gasification

raw CFB biosyngas

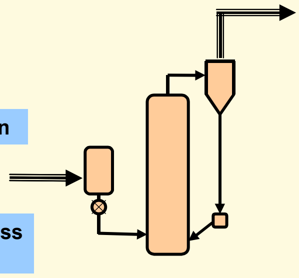
Main Constituents	*[vol%, dry]*	*[LHV%]*
CO	18	27.8
H_2	16	21.1
CO_2	16	-
N_2	42	-
CH_4	5.5	24.1
C_2H_4 (ethene)	1.7	12.4
C_2H_6 (ethane)	0.1	0.8
BTX	0.53	10.5
sum of tars	0.12	2.8
TOTAL	*100*	*100*

Impurities	*[mg/m$_n^3$]*
NH_3	2200
HCl	130
H_2S	150
all COS, CS_2, HCN, HBr	< 25
dust, soot, ash	2000

dilution (N_2)

energy loss for FT (CH_4, C_2H_4, C_2H_6, BTX)

catalyst poison (impurities)



CFB gasifier, 850°C, air-blown, atmospheric wood; 15 wt% moisture

Front-end Approach

economic considerations

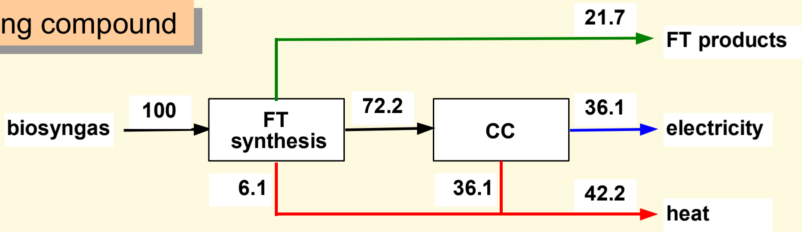
- scale: available gasifiers; 10-100 MW$_{th}$
- air-blown gasifier *(air separation is expensive)*
- no recycle *(due to N_2 in gas)*
- no CO_2 removal *(expensive)*
- no adjustment of H_2/CO ratio *(simplicity)*

Thus, operated in once-through mode: ***tri-generation***

Base-case

production of liquids, electricity, and heat

H_2 is limiting compound



Yield FT products = 100 × **33.5%** × 90% × 80% × 90%

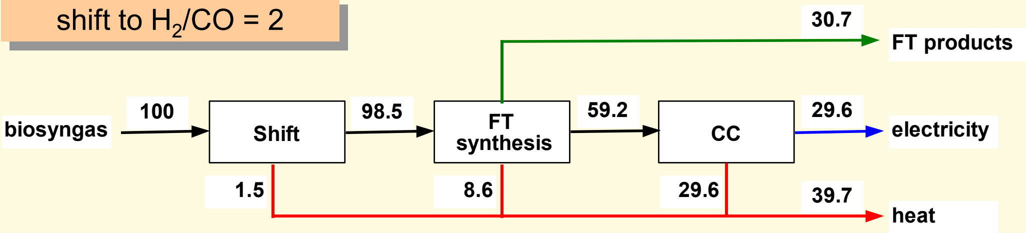
H_2/CO ratio = 0.89 *(containing 49% of the chemical energy)*

- energy content of product gas used for FT synthesis: 33.5%
- FT conversion, once-through: 90% (of limiting compound)
- heat generated: 20% of converted energy
- FT selectivity to C_5+ products (wax and liquids): 90%
- electrical efficiency CC: 50%
- assume clean gas and tars as inert

Importance of H_2/CO ratio

maximising conversion

shift to H_2/CO = 2



Yield FT products = (100-1.5) × **48.2%** × 90% × 80% × 90%

- energy content of product gas used for FT synthesis: 48.2%
- FT conversion, once-through: 90% (of syngas)
- heat generated: 20% of converted energy
- FT selectivity to C_5+ products (wax and liquids): 90%
- electrical efficiency CC: 50%

Gas Cleaning

general remarks

- state-of-the-art gas cleaning = for gas engine
  - *2 g/m_n^3 tars, tar dewpoint ~40°C*
- ! required: removal of organic compounds below dew-point
  - *2 ppmV naphthalene, 2500 ppmV BTX (@40 bar)*
- conventional wet gas cleaning is sufficient for NH_3, H_2S, etc.
  - *wet scrubbers & active carbon and ZnO guard beds*
- ! active carbon also captures BTX - not preferred!

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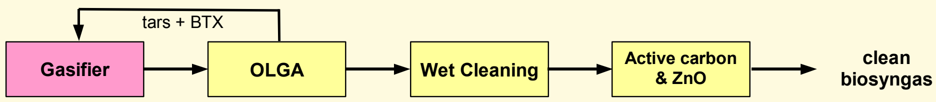
Design of Gas Cleaning (1)

are tars the issue?

- removal of BTX is strongly preferred
- tars are readily removed under BTX removal conditions
- ➨ Thus, the removal of BTX is the issue in gas cleaning

Process line-up:



Details on the novel and powerful OLGA technology for complete tar removal are presented in the poster session

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Back-end Approach

maximised production FT liquids

- scale: economically desired for FT unit; ~1000 MW_{th}
- electricity is by-product
- FT off-gas recycled *(oxygen-blown gasifier required)*
- CO_2 removal required
- adjustment of ratio $H_2/CO = 2$
- high H_2+CO yield *(tar cracker)*

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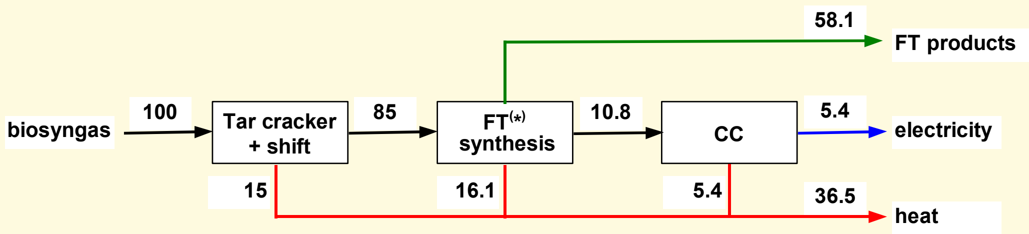
Importance of H_2+CO yield

maximising FT production

all CH_4 (24%), C_xH_y (12%), and BTX (11%) converted, and all tar cracked



Yield FT products = (100-15) × **100%** × 95% × 80% × 90%

- energy content of product gas used for FT synthesis: 100%
- FT(*) conversion, including recycle: 95% (of syngas)
- CO_2 removal
- and shift to $H_2/CO = 2$
- oxygen-blown gasification

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Design of Gas Cleaning (2)

maximised H_2+CO yield

- high-temperature step, *i.e.* tar cracker
- all BTX and tars are also removed/destructed

➡ Thus, conversion of all chemical energy into H_2+CO

Process line-up:

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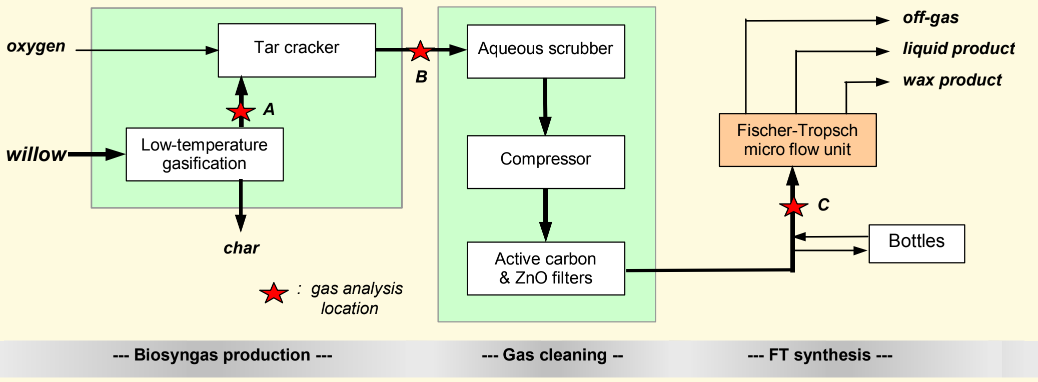
Integrated Test

process line-up



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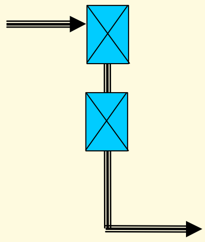
Demonstration

gas cleaning for large-scale systems

Gas		Raw biosyngas	Cracked biosyngas	FT feed gas
CH_4	[vol%]	6.42	0.01	0.01
C_2H_4	[ppmV]	5936	< 5	< 5
C_2H_6	[ppmV]	7359	< 5	< 5
BTX	[ppmV]	1266	< 5	< 5
Tars	[ppmV]	+/- 50%	< 10	< 10
NH_3	[ppmV]	~	516	0.02
H_2S	[ppbV]	~	23789	< 10
COS	[ppbV]	~	47578	278
CS_2	[ppbV]	~	207	< 10
TOTAL	*[vol%]*	*100.0*	*100.0*	*100.0*

(Experimental data)



1. high-temperature tar cracker
2. wet scrubbers
3. active carbon en ZnO guard beds

Technical Feasibility

demonstration of integrated system

Two tests for 150 h and 500 h:

1. gasification of willow

2. cleaning of biosyngas to FT specifications

3. operating a micro-flow FT unit on the cleaned gas

Successful:

- No loss of catalyst activity
- Constant gas consumption and off-gas composition
- FT products similar to fossil equivalents

"Product in Bottle"

Conclusions

insights on gas cleaning and process design

- BTX are the design guide line for gas cleaning *(not tars)*
- H_2/CO ratio in raw biosyngas is irrelevant
- Tar cracker is required for high FT yields *(high H_2+CO yield)*
- Oxygen-blown gasification is required (with a CFB) for high syngas conversions *(to allow a recycle)*
- Scale of the plant determines line-up of gas cleaning
- Technical feasibility of gas cleaning for BG-FT is successfully demonstrated

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