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Chair EVT



XtL: Development of synthesis fuels in Europe and South Africa

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I Introduction

- Global boundary conditions for synthetic fuels applications
- Indirect vs. direct coal liquefaction
- II Direct coal liquefaction and ist commercial applications
- III Development trends





Germany/Europe:

- No CtL (still very limited activities for shale gas) or GtL applications in Germany or Europe
- Conceptual studies on annex CtL blocks attached to conventional power plants in Germany
 Option for reduction of investment costs
 - \rightarrow Potential to include renewable hydrogen (storage of excess renewable electricity)
- Visible trend towards underground coal gasification in Poland and UK (but not for CtL)
- Politically driven development and demonstration of BtL routes

Africa:

- No new CtL developments in South Africa
- GtL development for flare gas utilization in particular in Nigeria (compact GtL)
- Trend towards underground coal gasification (but not for CtL)

Asia:

Continuous development/demonstration/commercialization of CtL and CtG technologies

Northern America:

Shale gas-to-liquids in the U.S.

Russia:

• GtL for flare gas reduction and consideration of CtL in remote areas







- High efficiency potential
- 1 commercial plant (Shenhua Direct Coal Liquefaction Plant located in Ordos/Inner Mongolia)
- 24,000 bpd (1 mill. t/a)

- More mature and established technology
- About 10 commercial plants with vaious synthesis technologies (FT, MtG etc.)
- Production capacity of >390,000 bpd (with the largest plant being operated in South Africa)





- I Indirect vs. direct coal liquefaction
- **II** Indirect coal liquefaction and its commercial applications
 - Introduction to the process chain
 - Major European process development in gasification
 - Major European process development in hydrocarbons syntheses
 - Examples of European BtL projects

III Development trends



Indirect coal liquefaction



















Status of commercially important European gasification technologies



Technology	Lurgi	BGL	Slemens	Shell	Prenflo	Choren
Max. realized capacity in t(coal)/d	1800 (Mark V Secunda)	1550 (Shriram Project)	1800 (NCPP Project)	2700 (e.g. Datang; Anning Yuntianhua)	2400 (Puertollano)	1500 (400 MW(th) GuiZhou- Province)
Max. planned capacity in t(coal)/d	2500 (Mark+) (=500 MW(th) for very low quality coal) * Turna, DGMK Tagung, 2012	1750 *Olschar, Gasification Course FG, 2012	2500 (currently only 2000 t/d = 850MW(th))	4000 (=1200MWth)	4000	2000
Number of gasifiers in operation	131 (excl SEDIN gasifiers)	4	9 (32)	20 plants with ca. 23 GW(th)	1	2
Major developments	Increase of single unit capacity, pressure and reduction of waste water yield	Adaptation to wider fuel range and customizing to application (fuel gas or syngas)	Increase of single unit capacity, feeding system and syngas cooling development	New syngas cooling concept (partial quench and convective cooling)	New syngas cooling concept (quench) and changed reactor layout	-/-



Indirect coal liquefaction







Fischer-Tropsch synthesis



Major chemical reactions:

 $\begin{array}{ll} \mbox{Paraffins:} & n\ CO + (2n+1)\ H_2 \leftrightarrow C_n H_{(2n+2)} + n\ H_2 O \\ \mbox{Olefins:} & n\ CO + 2n\ H_2 \leftrightarrow C_n H_{2n} + n\ H_2 O \\ \mbox{Alcohols:} & n\ CO + 2n\ H_2 \leftrightarrow C_n H_{(2n+1)} OH + (n-1)\ H_2 O \\ \mbox{Acids:} & C_n H_{(2n+1)} OH + H_2 O \leftrightarrow C_{(n-1)} H_{(2n-1)} COOH + 2\ H_2 \\ \mbox{Aldehydes:} & C_n H_{(2n+1)} OH \rightarrow C_{(n-1)} H_{(2n-1)} COH + H_2 \end{array}$

FT product spectrum dependent on catalyst properties



Chain growth probapility Source: Vertes, A. et al. "Biomass to Synfuels" Wiley 2010 Steynberg, A., Dry, M. "Fischer-Tropsch Technology" Elsevier 2004

HT-FT process layout



FT product spectrum dependent on temperature

Process	Temperature	Catalyst	Prefered product
HT-FT	ca. 350°C	Iron based	Gasoline/olefines
MT-FT	ca. 275 $^\circ$ C	Iron based	Diesel
LT-FT	ca. 230 ° C	Cobalt based	Diesel/waxes





SAS reactor scheme





Process characteristics:

High-temperature FT synthesis

Fluidized-bed reactor with iron-based catalyst

■Temperature: 330–350 °C

Pressure: max. 40 bar

Diameter: 10 m

Internal cyclones for catalyst recirculation

Products:

 Lighter components up to C₂₀ olefins and aromatics for gasoline and chemicals

References:

Secunda Sasol II and Sasol III, total capacity 160,000 bpd





SAS reactor scheme





Process characteristics:

- High-temperature FT
- Circulating fluidized-bed reactor
- Iron catalyst
- Tempartue/pressure: 340 ° C, 20 bar
- Syngas conversion of 80–90 %
- Capacity of 2500 bpd per reactor
- In Secunda: reactors later replaced by SAS reactors

Products:

Mainly for gasoline production

References:

 PetroSA: 45,000 bpd GtL facility in Mossel Bay (SA)





Slurry-phase reactor scheme



LT-FT synthesis loop



Process characteristics:

- Low-temperature FT synthesis
- Slurry-phase reactor
- Mainly cobalt-based catalyst
- Temperature: 200–240 ° C
- Pressure: 20-30 bar
- Diameter: 5 m
- 2,500 bpd per reactor

Products:

 Mainly wax and paraffines for diesel production

References:

- Sasolburg
 - 5,600 bpd
 - Switched from coal to natural gas in 2005

 ORYX GTL in Qatar (cooperation with Qatar Petroleum) 34,000 bpd

Source: "Sasol: an industrial perspective" UKZN 2013 Steynberg, A., Dry, M. "Fischer-Tropsch Technology" Elsevier 2004





SMD reactor scheme





Process characteristics:

- Low-temperature FT
- Fixed-bed multi-tubular reactors
- (similar to Sasol's ARGE)
- Cobalt-based catalyst

Products:

- Heavy Paraffin Synthesis (HPS)
- Maximal chain growth

References:

- Pearl GTL Qatar: 140,000 bpd
- Bintulu GTL Malaysia: 12,500 bpd





LT-FT reactor scheme





Process characteristics:

- Joint venture by PetroSA and Air Liquide
- Low-temperature FT synthesis
- Slurry bubble column reactor
- Cobalt-based catalyst

Products:

Naphtha, diesel and LPG from waxes

References:

 Semi-commercial demo plant in Mossel Bay (SA) (1,000 bpd oil or wax)





Gasel (Axens & ThyssenKrupp)



Process characteristics:

- Low-temperature FT-synthesis
- Slurry bubble column reactor
- Cobalt-based catalyst

Product:

Diesel

References:

- 20 bpd Pilot Plant in Sannazarro, Italy (20 bpd)
- Planned BioTfueL project for production of Biodiesel

Source: "Conversion of syngas to diesel" Axens Website June 2014

BP & JM Davy fixed-bed FT synthesis



Process characteristics:

- Low-temperature FT process
- Fixed-bed multi-tubular reactor
- Cobalt-based catalyst

References:

Pilot plant in Nikiski (Alaska)

Source: "Fischer-Tropsch Technology" BP website June 2014





Plant		Technology	Capacity (bpd)	Owner	Production start
Secunda	CTL	SAS	160,000	Sasol	1980/1984
Pearl	GTL	Shell MDS	140,000	Shell	2011
Mossel Bay	GTL	Synthol	45,000	PetroSA Statoil Lurgi	1992
Oryx	GTL	SPD	34,000	Qatar Petroleum Sasol	2007
Bintulu	GTL	Shell MDS	12,500	Shell	1993
Sasolburg	GTL	SPD	5,600	Sasol	1955
Ordos	CTL	Synfuels China MT-FT	4,000	Yitai	2009
ChangZhi	CTL	Synfuels China MT-FT	4,000	ShanXi LuAn	2009
Ordos	CTL	Synfuels China MT-FT	5,000	Shenhua	2009



Methanol-based fuel production



- TIGAS Topsøe Integrated Gasoline Synthesis MtG Methanol-to-Gasoline (ie.g. ExoxonMobil (Uhde))
- DtG Dimethylether-to-Gasoline (e.g. Karlsruhe Institut für Technology)
- DtO Dimethylether-to-Olefins (e.g. Karlsruhe Institut für Technology)
- MtO Methanol-to-Olefins (e.g. UOP, MtP®
 - by Lurgi/Air Liquide)

- StF Syngas-to-Fuel (CAC, TU Freiberg)
- MtD Methanol-to-Dimethylether (e.g. Lurgi/ Air Liquide)
- StD Syngas-to-Dimethylether (e.g. JFE)
- COD Conversion of Olefins to Distillates (e.g. Lurgi/ Air Liquide)
- MtS MtSynfuels® by Lurgi/Air Liquide

 $\begin{array}{l} 2 \ CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \\ CH_3OH, \ CH_3OCH_3 \rightarrow Light \ Olefins, \ H_2O \\ Light \ Olefins \ \rightarrow C_{5+} \ Olefins \\ C_{5+} \ Olefins \rightarrow Paraffins, \ Naphthenes, \ Aromatics \end{array}$

Source: Bertau, M. et al. "Methanol: The Basic Chemical and Energy Feedstock of the Future " Springer 2014, Stahlschmidt, R. "Concepts for XtL-Routes based on a technical proven Gasoline Synthesis Process" IFC 2014 Methanol to Gasoline (MTG)" ExxonMobil website June 2014







Process characteristics:

Ist stage: adiabatic fixed-bed reactor for DME production (300–420 ° C, 26–27 bar, aluminabased catalyst)

■2nd stage adiabatic fixed-bed reactor, ZSM-5 catalyst, (350-420 ° C, 19–23 bar), to be discontinuously regenerated Source: Bertau, M. et al.,

References:

- Jincheng MtG plant (China): 2,500 bpd
- Planed: Medicine Bow project (USA): 15,000 bpd

Source: Bertau, M. et al. "Methanol: The Basic Chemical and Energy Feedstock of the Future " Springer 2014, " Methanol to Gasoline (MTG)" ExxonMobil website June 2014





Fixed-bed MtG process layout





STF characteristics:

•Syngas \rightarrow Methanol \rightarrow Gasoline (direct processing of raw methanol from 1st stage)

Isothermal gasoline synthesis reactor layout

- \rightarrow improved stability and product quality
- •Application of newly developed catalysts for gasoline production and treatment of process water (formed in process) \rightarrow higher product yields and reduced waste water yield

Reduced amount of circulation gases in combination with isothermal plant operation







Process modifications

MTG process:

- Methanol as isolated intermediate, directly converted to raw gasoline
- Parallel adiabatic fixed-bed reactors
- Zeolite type catalyst GSK-10

STG process:

- Simultaneous formation of Methanol and DME without separation
- Especially suitable for syngas with H₂:CO near 1 (from coal, biomass)





Two-stage technology

- Addition of the dehydration stage to methanol production, e.g. Lurgi MegaDME, Topsøe's DME
- Problem: costs for cryogenic DME separation



Single-stage technology:

- Application of multifunctional catalysts (methanol synthesis and dehydration, water gas shift)
- Slurry reactor technology
- No commercial applications
- OEMs: JFE and Air Products



Source: Bertau, M. et al. "Methanol: The Basic Chemical and Energy Feedstock of the Future " Springer 2014, Zwiefelhofer, U., Liebner, W. "Monetisation of Gas and Coal as Feedstok for Petrochemicals through MtC" Gastech 2008 Bangkok Ohno, Y. "New Clean Fuel DME"DeWitt Asia Pacific Global Methanol & MTBE Conference 2008





Decentralized:

- Fast pyrolysis (sand as heating agent) of dry biomass at 500 ° C
- ■500 kg/h pilot plant

Centralized:

- Lurgi MPG-based gasification (1200 ° C, up to 80 bar)
- HT gas cleaning
- •Two-stage gasoline synthesis (DME as intermediate) with CAC
 - First stage: 250 $^\circ\,$ C, 55 bar
 - Second stage: 350 ° C, 25 bar, zeolitic catalyst
- 2MW(th) pilot plant at KIT in Karlsruhe (Germany)









- Joint project of: ThyssenKrupp Uhde, Axens, CEA, IFP Energies nouvelles, Sofiprotéol, Total
- Pilot plant in Venette and Dunkirk (3 t/h biomass torrefaction, 15 MW(th) gasifier), production scheduled for 2014

Process steps:

- Biomass pre-treatment and torrefaction at 250–300 ° C
- Prenflo PDQ gasification (1200–1600 ° C, 30–42 bar)
- Syngas cleanup
- Gasel Fischer-Tropsch by Axens (1st pilot-scale demonstration)







- DME production from pulp mill residuals
- Chemrec black liquor Gasification (entrained flow, top-fired, 30 bar, 1050 ° C)
- Haldor Topsoe two-stage DME technology
- 38 bpd plant in Pitea, Sweden (2011)









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Reduction of investment costs:

- Simplification of technology
- Increase of unit size
- New gasifiers and components:
 - Compact gasifiers (Aerojet Rocketdyne (former PWR))
 - Mild Gasification (INCI)
 - Solid feed pumps (Aerojet Rocketdyne (former PWR), GE)
 - Advanced refractory materials
- Increase of efficiency and matching raw gas composition to application:
 - Increase carbon conversion
 - Tendency to dry feed systems (slurry drying or solid feed pumps)
 - Flexibilization of heat recovery systems

Besides: Significant increasing efforts to further develop gas-to-syngas technologies (e.g. for flare gas or smaller-scale shale gas application)





- FT routes for diesel production and methanol-based routes for gasoline
- In western countries only consideration of synthesis products competing with oil products
- Strong trend for GtL in the U.S. and upcoming trend for small-scale technologies for flare gas and associated gas utilization
- Synthesis development requirements:
 - Tailored products pectrum (catalyst and operation conditions)
 - Optimized reactor concepts

- \rightarrow reduction of refining efforts
- \rightarrow reduction of cooling effort
- \rightarrow reduction of equipment effort
- Reduction of waste water yield
- Scale-down of single unit size allowing for off-shore or small-scale applications for flare gas/associated gas utilization



Thank you for your attention!













Features:

- Semi-continuous feeding via sluice system (optional coal distributer)
- Water jacket with outer steel pressure shell and inner temperature shell (for corrosive ashes SiClined)
- 10–15 % of gasification agent steam generated in water wall
- Inner diameter 2.6–4.7 m, height 5-9 m
- O₂/H₂O injection by rotating grate while ash is cooled to 300–400 ° C
- Gas exit temperature 370-600 ° C
- Production of tar/dust/water mix in wash cooler
- → 7 Plants (153 gasifiers) operating
 17.9 GW (th)
 FT-fuels; SNG; Fertilizer; MeOH; Reduction gas



Source: Peter Modde und Steffen Krzack. Die Veredlung und Umwandlung von Kohle, Technologien und Projekte 1970 bis 2000 in Deutschland, Chapter: Gaserzeuger mit Drehrost, Seiten 307–309. DGMK, 2008; Weiss, M.-M.: Update on New Project & Design Developments with Lurgi's FBDB Gasifier, CCT 2011.





Commercial plants:

131 gasifiers in operation (excl. domestic Chinese (SEDIN) FBDB gasifiers)

26

14

5

2

80+4

- Vresova
- Sasol Synfuels, Secund, SA
- Dakota Gasification Company, Dakota, USA
- Shanxi-Tianji Coal Chemical Company, CHN
- Yima, CHN
- Current activities Lurgi FBDBTM:
 - Jindal Steel & Power, Angul plant
 225,000 Nm³/hr syngas from 7 gasifiers, start up 2013
 - Projects under developments Lurgi FBDB[™]:
 8x Coal to SNG 7x Coal to Liquids
 3x Coal to Chemicals 1x Coal to MeOH
 4x Coal to Fertilizer 1x Coal to Power
- Next technology steps Lurgi FBDBTM:
 - Lurgi FBDB[™] Mk Plus[™] (60 bar, twin coal lock, 5.05m outer diameter)
 - Reduction of water consumption (e.g. dry ash handling)

Power
Liquid fuels & chemicals
SNG
Ammonia
MeOH





Commercially important gasification technologies British Gas/Lurgi Gasifier (BGL) – Envirotherm, ZEMAG, Advantica



Features:

- Upper part like Sasol-Lurgi-FBDB
- Semi-continuous feeding via a double sluice system
- Water jacket with outer steel pressure shell and inner shell with refractory lining (MgO, SiC)
- Slag bath (1250-1500° C) with cooling tubes and protective solid slag layer
- Inner diameter 3.6 m, height 12-13 m
- O₂/H₂O injection by 6 tuyere nozzles
- Natural gas ring burner to keep slag tap open
- Gas exit temperature 500-800 ° C
- Production of tar/dust/water mix in wash cooler
- References plants location: SVZ Schwarze Pumpe (GER), Hulunbeier (CHN), Luoyang (CHN), Orissa (IND), Ordos Tuke (MNG)



Source: Turna, O. et al.: Die Veredlung und Umwandlung von Kohle, Technologien und Projekte 1970 bis 2000 in Deutschland, Chapter British Gas/Lurgi-Schlackebad-Vergaser (BGL), Seiten 363–391. DGMK, 2008. M. Olschar,5th International Freiberg Conference, 2012





Features:

- Upward single-stage pressurized entrainedflow gasification (24-40 bar)
- Dry feeding via lock hoppers + dense-phase conveying
- Outer steel pressure vessel with inner membrane wall (2–4 % loss LHV input)
- Gas residence time: 0.5–4 s
- Coal + O₂/H₂O injection typically four twoflow burners in boxer arrangement
- Direct dust recycle by cyclone
- Gas exit temperature 1500 ° C
- Raw gas cooling by cold recycle gas quench to 900 ° C (50 % gas recycle necessary)
- → 20 Plants operating on solid feedstocks approx. 23 GW (th)

Source: Radtke, K., Rich, J.W. Jr., Hoppe, R.: Indirect Coal Liquefaction - Shell Coal Gasification with Fischer-Tropsch Synthesis. 1st International Freiberg Conference on IGCC & XtL Technologies, 2005. S. van Paasen, Technology Development for Shell coal gasification, IFC, 2012





Commercially important gasification technologies



Shell Gasifier (Prenflo Gasifier)



Adapted from: Higman, C. and van der Burgt, M.: Gasification. Elsevier Science, New York, 2003. ISBN 978-0-75-067707-3; Radtke, K., Rich, J.W. Jr., Hoppe, R.: Indirect Coal Liquefaction - Shell Coal Gasification with Fischer-Tropsch Synthesis. 1st International Freiberg Conference on IGCC & XtL Technologies, 2005. and Volk, J.: Coal Gasification: Delivering Performance in Chinese Operations & Developing Technology Deployment Solutions. Gasification Technologies Conference, 2010.





Differences between Shell and Prenflo plant setup



Adapted from: Eurlings, J. and Ploeg, J.: Process Performance of the SCGP at Buggenum IGCC. Gasification Technology Conference, 1999.; Radtke, K.: Uhde Biomass and Coal Gasification: Applying Fluidized Bed and Entrained Flow Gasification. Gasification Technologies Conference, 2010.; Mendez-Vigo et al.: The Puertollano IGCC Plant: Status Update. 1998.; Volk, J.: Coal Gasification: Delivering Performance in Chinese Operations & Developing Technology Deployment Solutions. Gasification Technologies Conference, 2010



Commercially important gasification technologies Shell Gasifier (Prenflo Gasifier)





Sources: Chhoa, T.: Radtke, K. and Heinritz-Adrian, M.: PRENFLO PSG and PDQ. Gasification Technology Conference, 2008.; Volk, J.: Coal Gasification: Delivering Performance in Chinese Operations & Developing Technology Deployment Solutions. Gasification Technologies Conference, 2010.



Commercially important gasification technologies Shell Gasifier (Prenflo Gasifier)



Illustrative Material



2000 t/d Shell gasifier before installation in pressure vessel



Membrane wall of Prenflo coal gasifier



Membrane wall of Prenflo coal gasifier

Sources: Chhoa, T.: Shell Gasfication business in action. Gasification Technologies Conference, 2005.; Radtke, K., Rich, J.W. Jr., Hoppe, R.: Indirect Coal Liquefaction - Shell Coal Gasification with Fischer-Tropsch Synthesis. 1st International Freiberg Conference on IGCC & XtL Technologies, 2005.; Radtke, K. and Heinritz-Adrian, M.: PRENFLO PSG and PDQ. Gasification Technology Conference, 2008.





Features:

- Downward single-stage pressurized entrained-flow gasification (5-25 bar)
- Dry feeding via lock hoppers + dense-phase conveying by N₂, CO₂ or natural gas
- Outer steel pressure vessel with inner coiled cooling screen (2.5 % loss LHV input)
- Refractory lined gasifier for low ash coals available (e.g. Vresova IGCC)
- Gas residence time: 2-4 s
- Coal + O₂/H₂O injection through one top central burner with integrated pilot burner
- Integrated spray water quench from 1300-1800
 ° C to saturation temperature (240 ° C)
- Slag granulation in water bath

References:

- 9 x 500 MW gasifiers installed in 3 projects (2 plants operating)
- 32 gasifiers under manufacturing





Commercially important gasification technologies Siemens Gasifier (SFGT or GSP)





Sources: Morehead, H.: Siemens Technology Advances and Project Development Activities. Gasification Technologies Conference, 2010. Schingnitz, M.: Übersichtsvortrag zur Vergasungstechnik. Technische Universität Dresden, 2010.





Development directions

- Scale up to 850 MW
- Raw gas cooling and heat recovery



Sources: Hannemann, F., Schingnitz, M. and Zimmermann, G.: Siemens IGCC and Gasification Technology - Today's Solution and Developments. 2nd International Freiberg Conference on IGCC & XtL Technologies, 2007.; Morehead, H.: Siemens Technology Advances and Project Development Activities. Gasification Technologies Conference, 2010.







Features:

- Roots back to GSP gasifier
- Multiple burners
- Two separate vessels

Projects:

- YanKuang project (GuiZhou, CHN)
 - Operating since 2013
 - 2+0 gasifiers (each 1,500 t/d coal)
 - 500,000 t/a ammonia
- Jarud project (CHN)
 - Start up 2015
 - 2+0 gasifiers (each 1,500 t/d coal)
 - 600,000 t/a ethylene glycol





Fischer-Tropsch (FT) synthesis

Preferably for production of diesel or jet fuel

- Low-temperature FT synthesis with syncrude (wax upgrading)
- Gasoline and olefines only applied in two plants
- High-temperature FT synthesis

 Combined diesel and gasoline synthesis with reduced product purification effort

➔ New medium-temperature FT synthesis (Synfuels China Technology Ltd. & Co.)

 All FT syntheses with high refining effort for products

Methanol-based syntheses

Production of:

- Gasoline
- Olefines / aromatics or
- DME (diesel substitute)

DME as intermediate product for most synthesis routes

Reduced product refining effort because of higher selecivity compared to FT syntheses





Fluid-bed MtG process layout



Process characteristics:

 Direct hydrocarbon formation in isothermal fluid-bed reactor with vaporized MeOH, continuous catalyst regeneration

Recovery of high-pressure steam

Improved economics because of lower investment costs

References:

Demo plant in Wesseling (Germany): 4,000 tpy

Never commercialized





MtSynfuel (Lurgi/Air Liquide)

- Based on MTP process (consecutive DME and propene production on zeolite catalyst)
- Further oligomerization and processing to gasoline and diesel (COD by PetroSA)
- Developed up to pilot plant scale

MOGD (ExxonMobil)

- Based on MTO process
- Products mainly i-olefins, need further hydrogenation
- Tested 1981 in a Mobil refinery



- Joint project of: UPM, Haldor Topsoe, Phillips66, Carbona, GTI
- Demonstration Plant at GTI in Des Plaines (IL), 20–25 bpd (2014)
- Process steps:
 - ANDRITZ/Carbona bubbling fluidized-bed gasification (10 bar, 850 ° C)
 - Syngas cleanup
 - TIGAS gasoline synthesis







