High quality (bio) fuels and chemicals via Fischer-Tropsch synthesis

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- Introduction to Fischer-Tropsch-synthesis:
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- Properties of Fischer-Tropsch fuels:
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  - How can they be upgraded ?
- Chemicals via FT-synthesis:
  - Light olefins
  - BTX and other possibilities
- CO_2 as the carbon source ?

Types of biodiesel

	FAME	Fossil diesel	HVO	Fischer-Tropsch
Raw material	Rapeseed or other vegetable oils	Mineral oil	Vegetable oils or waste fats (animal or vegetable)	Biomass, wastematerials
Process	Esterification	Refinery	HDO	Gasification + FT
Product	1st generation biodiesel	Hydrocarbon	Aliphatic hydrocarbon	Aliphatic hydrocarbon
Compounds	Esters	Hydrocarbons	Hydrocarbons	Hydrocarbons
Commercial availability	Very limited	Yes	Yes	FT-diesel Yes, from biomass No

General properties of biodiesels

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FAME	HVO	FT
Methyl esters	Hydrocarbons	**Hydrocarbons**
• Restricted blending with fossil fuel (<7 vol-%, EN590) • Limited long-term stability • Heat value 37-38 MJ/kg • Not suitable as jet fuel	• Compatible with all vehicles • Can be blended • Stable • Heat value >42 MJ/kg • Emission reduction • Can be refined to any fuel	• **Compatible with all vehicles** • **Can be blended** • **Stable** • **Heat value >42 MJ/kg** • **Emission reduction** • **Can be refined to any fuel**

Gasification

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Wide Feedstock Basis

- Oil
- Coal
- **Biomass**
- Waste/SRF

$(CO + H_2)$

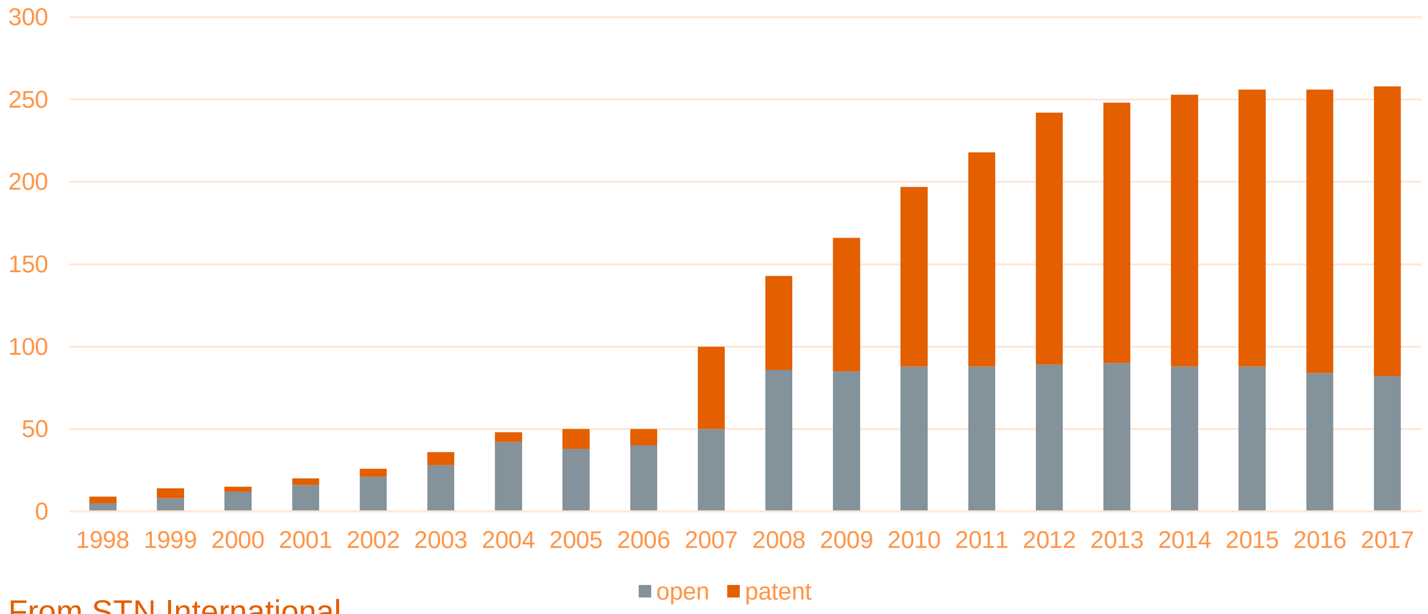
O_2 Air Steam

FT-diesel fuel
Methanol, DME
Gasoline, jet-fuel
Hydrogen
Synthetic methane
Chemicals

Industrial kilns
co-firing in boilers
Gas turbines
Engines
Fuel cells

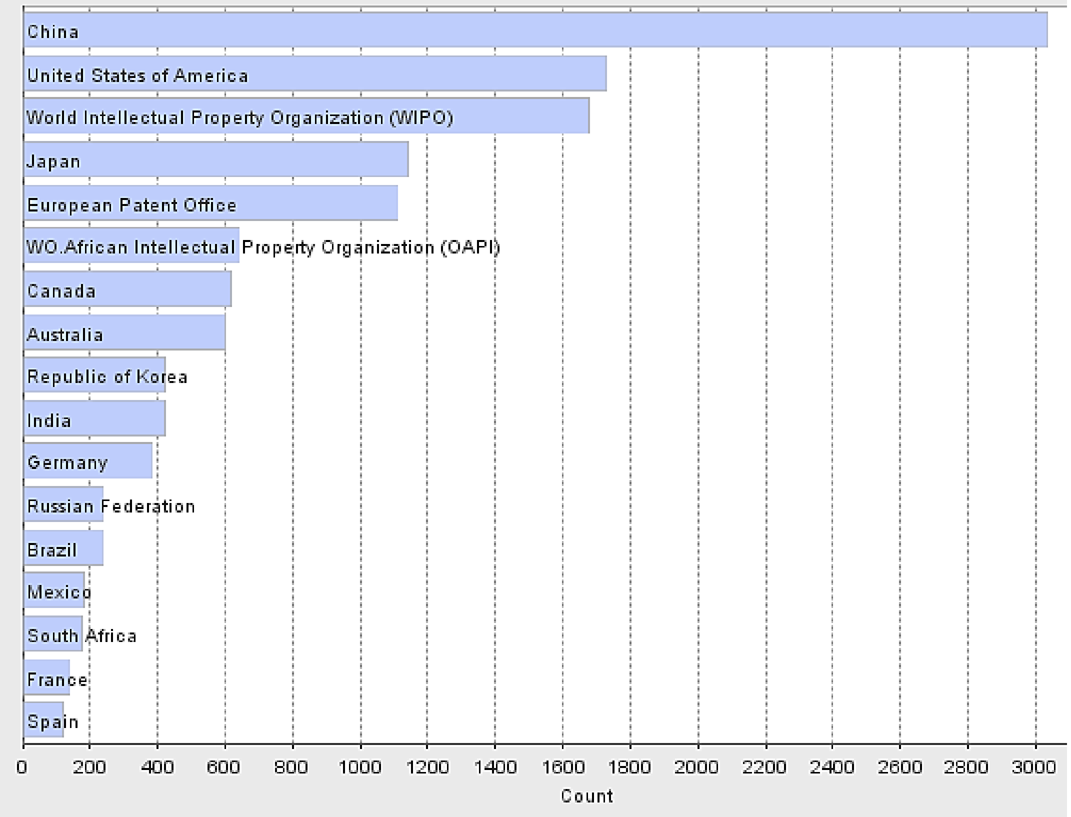
High quality final products

Biomass gasification to fuels: Indicative trend of number of patents and open publications / year



From STN International

Biomass gasification to fuels/chemicals: patent countries



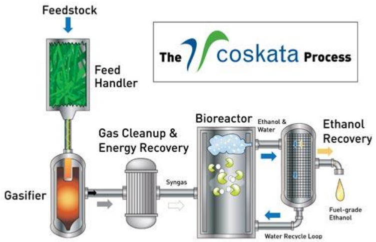
Existing biomass-based plants

A good source for current status of:

- Biomass gasification based
- Biomass pyrolysis based and
- Thermochemical / biotechnical hybrid plants and demo projects

can be found at http://demoplants.bioenergy2020.eu

supported by the IEA Bioenergy Task 39 – Commercializing Conventional and Advanced Transport Biofuels from Biomass and Other Renewable Feedstocks



Biomass as raw material for the synthesis gas route

- In principal, syngas reactions are not dependant on the raw material, but relevant differences still exist:
  - There is less experience in biomass gasification
  - Biomass gasification plants are generally at least one order of magnitude smaller than coal or natural gas fueled plants:
    - For instance Shell-Pearl GTL-plant 140 000 bpd; 400 MW BTL-plant would be ca. 4 000 bpd
  - Gasification and gas cleaning constitute a decisive part of the investment cost
    - Loss of economy of scale
  - Different kind of impurities (tars, ca. 100 ppm sulphur…)
  - Variation in the H/C ratio
  - Product upgrading (best product in small scale?)

Short history of the Fischer-Tropsch synthesis

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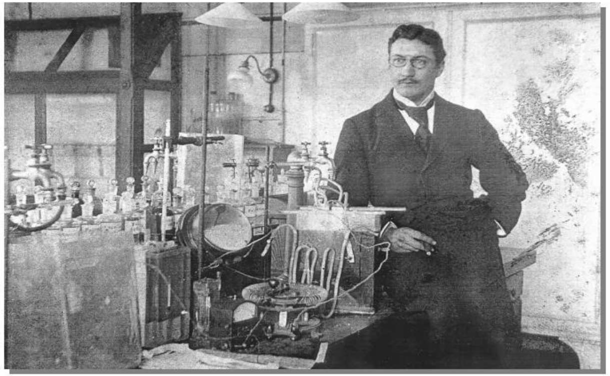
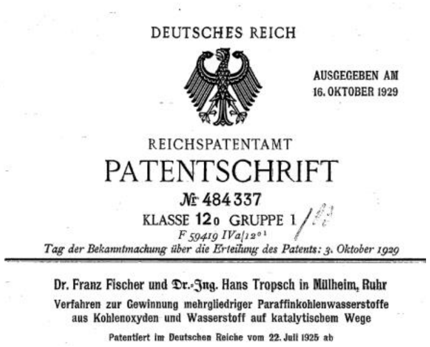
Franz Fischer at Work in 1918



Financial Mail, 2000



DEUTSCHES REICH

AUSGEGEBEN AM 16. OKTOBER 1929

REICHSPATENTAMT

PATENTSCHRIFT

№ 484337

KLASSE 12o GRUPPE 1

F 59419 IVa/12o¹

Tag der Bekanntmachung über die Erteilung des Patents: 3. Oktober 1929

Dr. Franz Fischer und Dr.-Ing. Hans Tropsch in Mülheim, Ruhr

Verfahren zur Gewinnung mehrgliedriger Paraffinkohlenwasserstoffe aus Kohlenoxyden und Wasserstoff auf katalytischem Wege

Patentiert im Deutschen Reiche vom 22. Juli 1925 ab

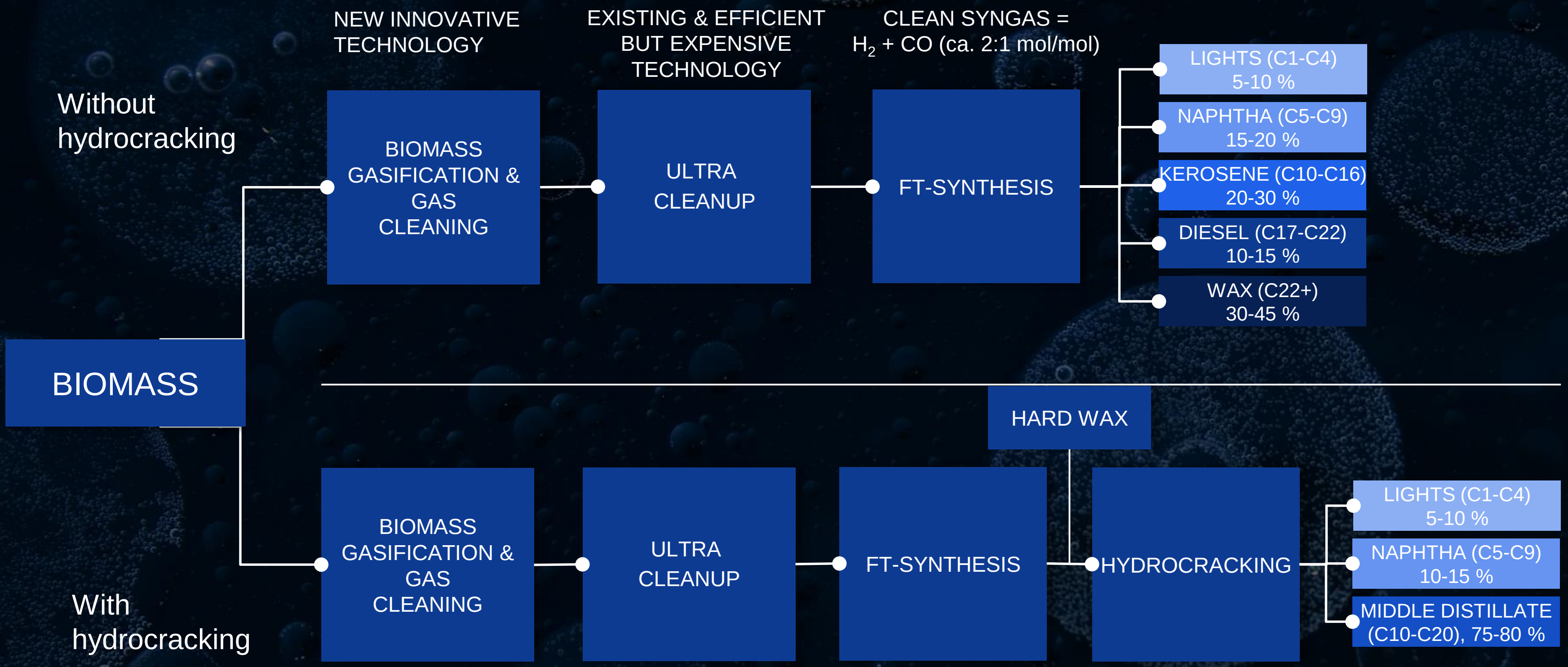
- 1902 Sabatier and Senderens: $CO+H_2$ -> CH_4 with Ni catalyst
- 1923 Fischer and Tropsch: $CO+H_2$ to liquid, Co, Fe and Ru catalysts
- 1925 First patent
- 1936 First commercial plant (Germany)
- 1944 Product peaks in Germany 16000 bpd, production also in Finland, raw material peat (catalyst of G. Komppa)
- 1947-53 Production in the USA
- 1955 Sasol 1 (800 bpd) in Southern Africa
- 1975 New plants in USA
- 1980 Sasol 2 (150 000 bpd), iron catalyst
- 1993 Shell Middle Distillate Process, Malesia
- 2000- Smallish BTL processes
- At the moment several large GTL and CTL projects

Reactions in the Fischer-Tropsch synthesis

- **Paraffin: $(2n+1)H_2 + nCO \text{ --> } C_nH_{2n+2} + nH_2O$**
- **This can be written also as a polyerisation of methylene monomer:**
  - **$(CO + 2H_2) \rightarrow -(CH_2-)_n + nH_2O$**
- Olefin: $2n\ H_2 + nCO \text{ --> } C_nH_{2n} + nH_2O$
- Alcohols: $2n\ H_2 + nCO + C_nH_{2n+1}OH + (n-1)\ H_2O$
- Shift: $CO + H_2O \text{ --> } CO_2 + H_2$
- Boudouard: $2CO \text{ --> } C + CO_2$
- Coke: $H_2 + CO \text{ --> } C + H_2O$

- Heterogeneously catalysed three phase reaction (gas-solid-liquid)
- Highly exothermic (deltaH = -165 kJ/mol)
- Restricted by mass transfer and heat removal
- Large amount of water (1.3 kg / 1 kg of HCs) is formed as a ”side”-product

Fischer-Tropsch-synthesis



Some challenges of the FT-reaction

- Even if you aim at producing diesel you get at least 25 % of other products and you must find good use for all of them
- High investment cost of the plant
  - Fairly complicated process
  - Cobalt catalysts used in the manufacture of FT-wax are very sensitive to sulphur and other impurities
- The reaction is highly exothermic and the reaction heat must be controlled and utilized

	AFS distribution of Fischer–Tropsch products			Calculated distributions of the two–stage concept	
Growth chance α	Percent by weight of			Percent by weight of	
	$<C_{10}$	$C_{10}-C_{20}$	$>C_{20}$	$<C_{10}$	$C_{10}-C_{20}$
0.80	62.4	31.8	5.8	63.6	36.4
0.85	45.6	38.9	15.5	48.7	51.3
0.90	26.4	37.1	36.5	33.7	66.3
0.95	8.6	19.8	71.7	22.9	77.1
0.98	1.6	4.9	93.5	20.3	79.7
0.99	0.4	1.4	98.2	20.0	80.0

Logistic challenge of a large plant

A 260 MW (effective fuel power) FT-plant integrated with a pulp and paper mill could produce about 105 000 metric tons of diesel fuel/year which equals ca. 3 % of Finnish transport fuel consumption. (About 5.2 kg of wood is needed for 1 kg of FT-product.)

A typical trailer truck used in Finland has a payload of about 35 metric tons or 115 m^3.

About 45-50 additional truckloads day of wood chips (moisture content 40 %) would be needed to feed a plant of this size

Typical composition of FT-crude (w-%)

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Product fraction	Carbon range	Compound class	Fe-HTFT	**Co-LTFT**
Tail gas	C1	Paraffin	12.7	**5.6**
	C2	Olefin	5.6	**0.1**
		Paraffin	4.5	**1.0**
LPG	C3-C4	Olefin	21.2	**3.4**
		Paraffin	3.0	**1.8**
Naphtha	C5-C10	Olefin	25.8	**7.8**
		Paraffin	4.3	**12.0**
		Aromatic	1.7	**0**
		Oxygenate	1.6	**0.2**
Distillate	C11-C22	Olefin	4.8	**1.1**
		Paraffin	0.9	**20.8**
		Aromatic	0.8	**0**
		Oxygenate	0.5	**0**
Residue/wax	>C22	Olefin	1.6	**0**
		Paraffin	0.4	**44.6**
		Aromatic	0.7	**0**
		Oxygenate	0.2	**0**
Aqueous product	C1-C5	Alcohol	4.5	**1.4**
		Carbonyl	3.9	**0**
		Carboxylic acid	1.3	**0.2**

Modified from:
Maitlis P. M., de Klerk A., Greener Fischer-Tropsch Processes for fuels and Feedstocks, Wiley-VCH, 2013, p. 83.

Fischer-Tropsch fuel properties

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- Highly n-paraffinic
  - Can be refined to very high quality fuels using existing techniques
    - For diesel n-alkanes have bad cold properties and isomerisation is needed
    - Density often lower than that of fossil fuel due to the lack of aromatics
    - For gasoline octane number needs to be increased by reforming
- No sulphur, no heavy metals or other catalyst poisons
- FT-product is always a mixture and always also gasoline and gases are produced
- In general, **quality is as good or better as that of fossil fuels**

Biocrude upgrading

FT BIOCRUDE

- LIGHTS (C1-C4)
- LIGHT NAPHTA (C5-C6)
- HEAVY NAPHTHA (C6-C9)
- MIDDLE DIST. (C10-C22)
- WAX (C23+)

WAX (C23+) → **FT WAX HYDROCRACKING**

- LIGHTS (C1-C4) 5-10 %
- LIGHT NAPHTA (C5-C6) 5-10 %
- HEAVY NAPHTHA (C6-C9) 10-15 %
- MIDDLE DISTILLATE (C10-C22), 75-80 %
- Unconverted fraction C23+

Feasible process can only be achieved if all fractions can be upgraded successfully at the refinery.

Process integration to oil refinery

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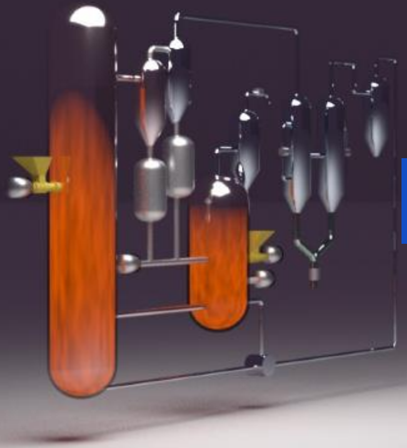
Refining must be planned according to the existing possibilities at the refinery. Take at look at a public report of EU-FLEXCHX-project: http://www.flexchx.eu/pdf/D7_1_Market_Review_Report_Feb_2019.pdf

BIOCRUDE FRACTIONS

- LIGHTS (C1-C4) → Petrochemical manufacturers
- LIGHT NAPHTA (C5-C6) → Steam cracking
- HEAVY NAPHTHA (C6-C9) → Continuous catalytic reforming
- MIDDLE DIST. (C10-C22) → New hydroisomerization unit
- Unconverted oil fraction (C23+) → Fluid catalytic cracking

Green BTX flexibly from biomass



Biomass → Gasification & Gas upgrading → FT-REACTION Fe-CATALYST High-T, low-P → BIO-α-OLEFINS C2-C16

Forestry residues,
mill residues,
straw,
energy crops,
urban biowaste

PCT/FI2016/050409
US2016237354A, WO15052379 A1,

PAO 4 €/kg	SYNTHETIC LUBRICATION OIL
ASA 4 €/kg	PAPER SIZING AGENT
EPOXIDES	REACTIVE MODIFIER FOR CELLULOSE, STARCH AND LIGNIN
BENZENE, TOLUENE XYLENE 0,5-1,2 €/kg	PLASTICS, FINE AND SPECIALTY CHEMICALS, PHARMACEUTICALS PAINTS, FIBRES, RESINS…
LINEAR POLYCARBONATES 3,5 €/kg	POLYCARBONATE PLASTICS
OXOALDEHYDES	LUBRICANT ADDITIVE, SURFACTANT, ACID SCAVENGER ,SOLVENT, RESIN MODIFIER, RESIN DRIER
ALKYLSILANES	SURFACE MODIFIER COMPATIBILITY AGENT

PCT/FI2016/050409, Method and apparatus for producing a chemical compound and a chemical compound and its use; TRL 3-4

US2016237354A, WO15052379 A1, Method and apparatus for producing a hydrocarbon fraction and a hydrocarbon fraction and its use

EARTO IMPACT DELIVERED

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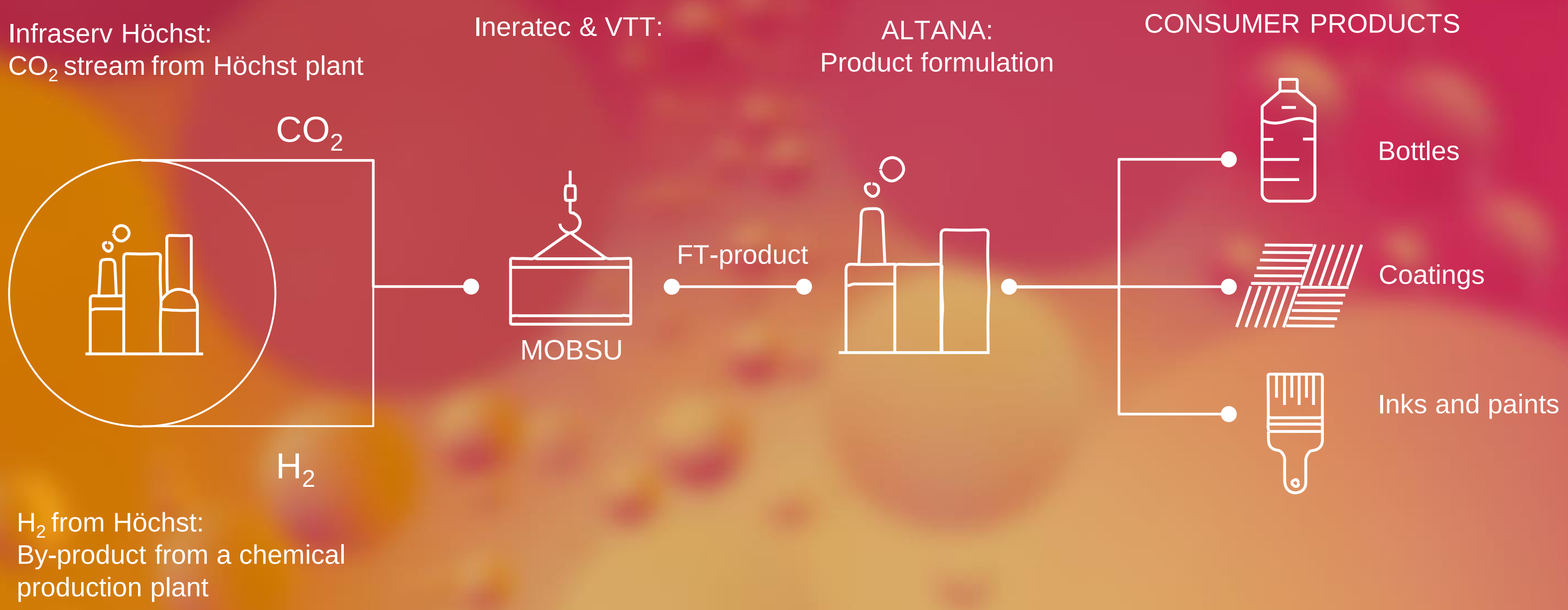
EARTO Innovation Award 2017 for Bio-BTX

CO_2 as a feedstock

Reverse Water gas shift (RWGS) reaction

$$CO_2 + H_2 = CO + H_2O \quad =>$$

https://www.spire2030.eu/ico2chem



beyond the obvious

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