Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes

Proceedings

6-30-2019

EN-fuels from solid waste biomass by thermo-catalytic reforming

Andreas Hornung

Andreas Apfelbacher

Robert Daschner

Nils Jäger

Jan Grundwald

EN-Fuels from solid waste biomass by thermo-catalytic reforming

Prof. Dr. rer. nat. Univ.- Prof. Dipl.-Ing. Andreas Hornung CEng FIChemE FRSC



Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes

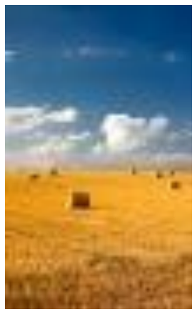
June 16 – 20, 2019 in Cork

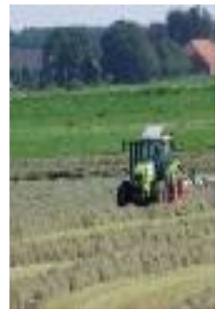
Fraunhofer
UMSICHT

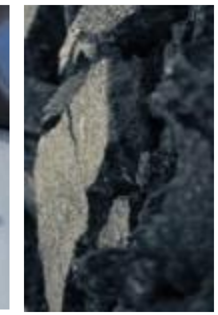
Recycling and Waste Management

TCR® und iCycle® – Technologies for Recycling & Energy Production

Biogenic Residues (TCR®)	Composites und Minerals (iCycle®)







Energy carrier from biomass & recycling of composites

General thoughts- How to store carbon by using fuel and producing plastics!

530 billion tonnes, 82 percent of all C in biomass (650 billion tonnes) on earth is stored in wood, the rain forest is storing as much as people burn in 10 years from various sources.

1/3 of world antropogenic CO_2 emissions are taken up every year by world wide forests.

But, CO_2 is also again released by natural processes

Carbon dioxide, naturaly captured in wood can be captured as carbon in char.

Feedstocks should show a wider range than wood only, residues from agriculture or sewage sludge and digestates as well as resdiues from modern processes producing ethanol from straw as well as macro algae

Capturing the carbon as a stabile bio-coal or charcoal as single product is just too expensive.

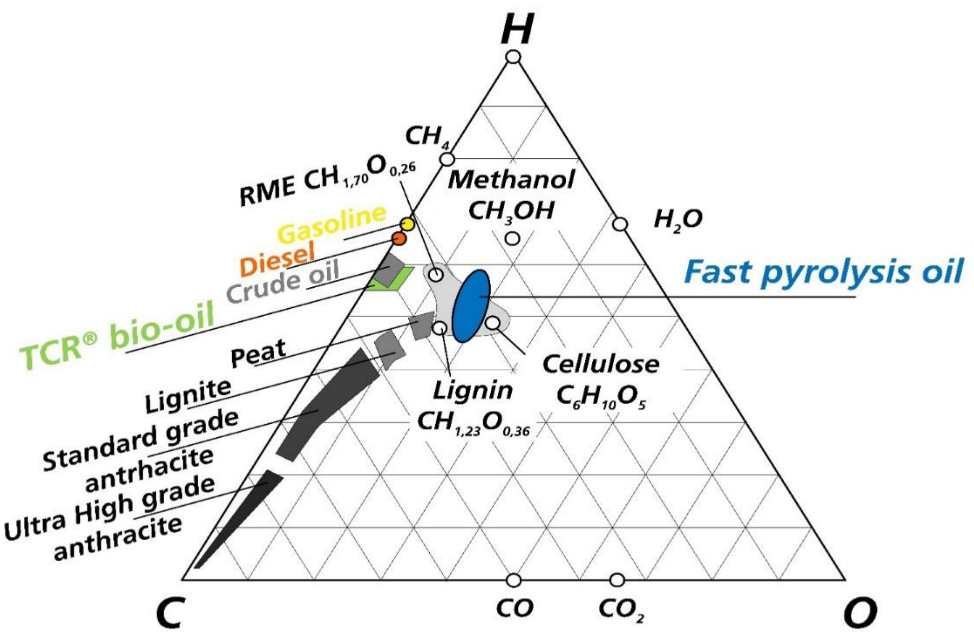
Side products are requried to close the bill.

Those products can be liquids, in best case fuels and green hydrogen.

Fraunhofer UMSICHT

Sustainable transportation of fuels by co-processing of TCR®-bio-oil in conventional petroleum refineries
Characteristics of TCR®-bio-crude-oil

- Compareable to crude oil
- High carbon content
- Low water content
- Low total acid number
- Miscible with fossile fuels and biofuels
- High heating value

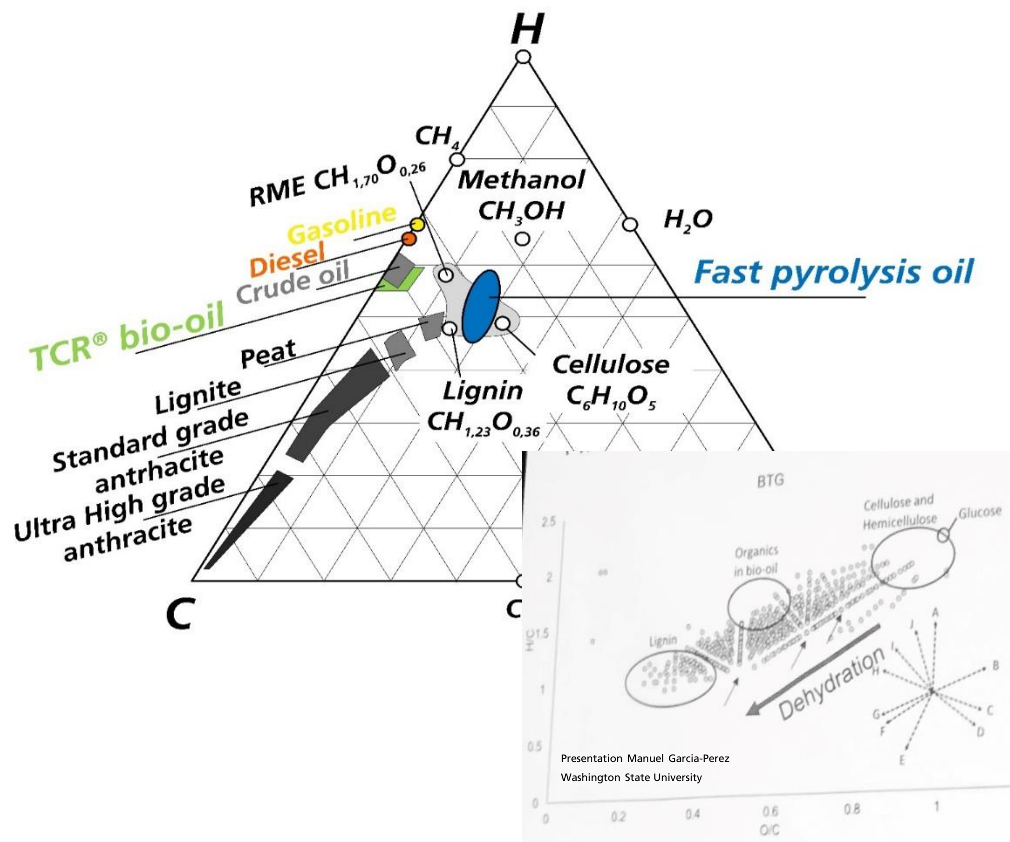


Source: [1] [2]

Sustainable transportation of fuels by co-processing of TCR®-bio-oil in conventional petroleum refineries

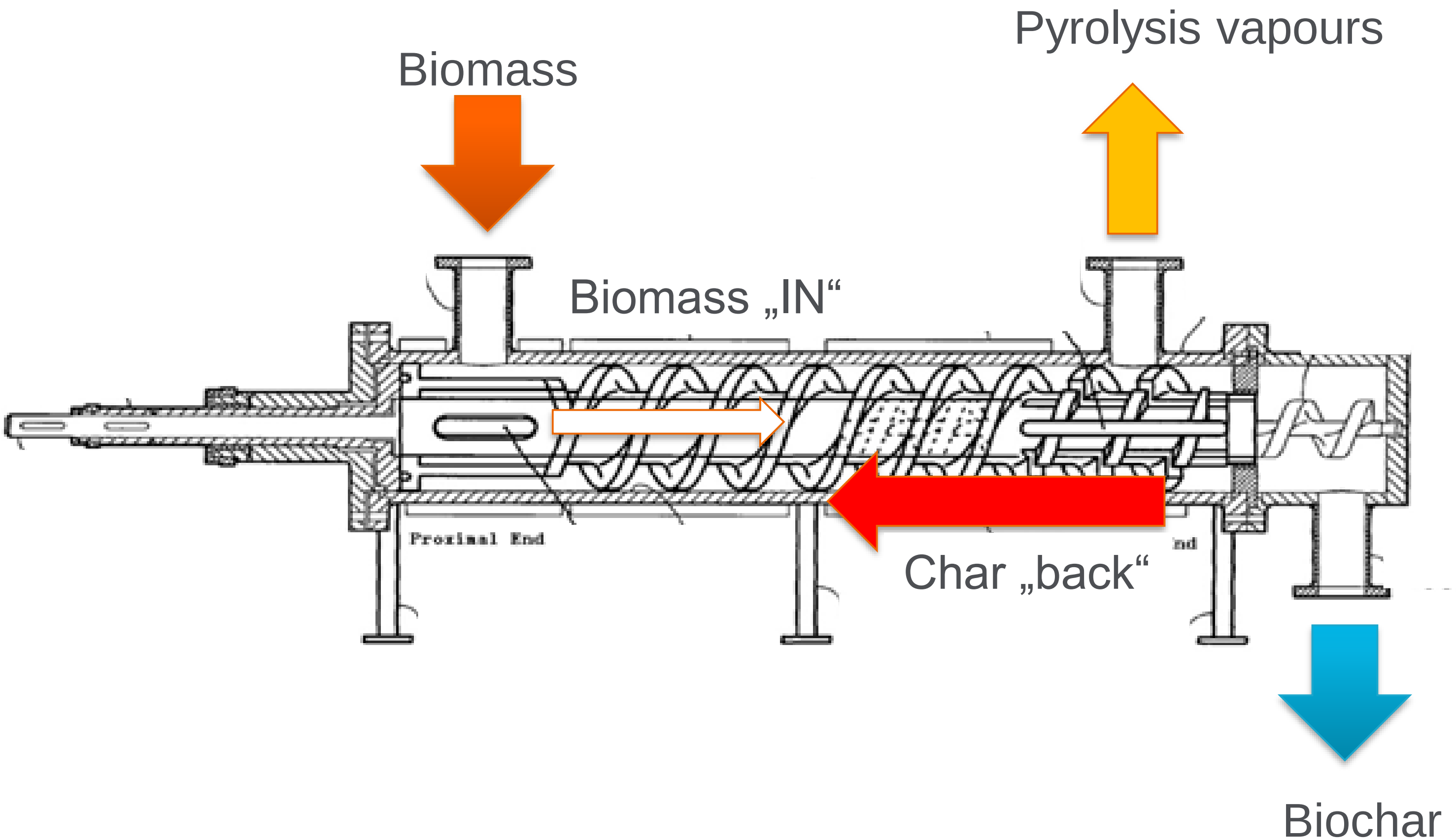
Characteristics of TCR®-bio-crude-oil

- Compareable to crude oil
- High carbon content
- Low water content
- Low total acid number
- Miscible with fossile fuels and biofuels
- High heating value



Fraunhofer UMSICHT

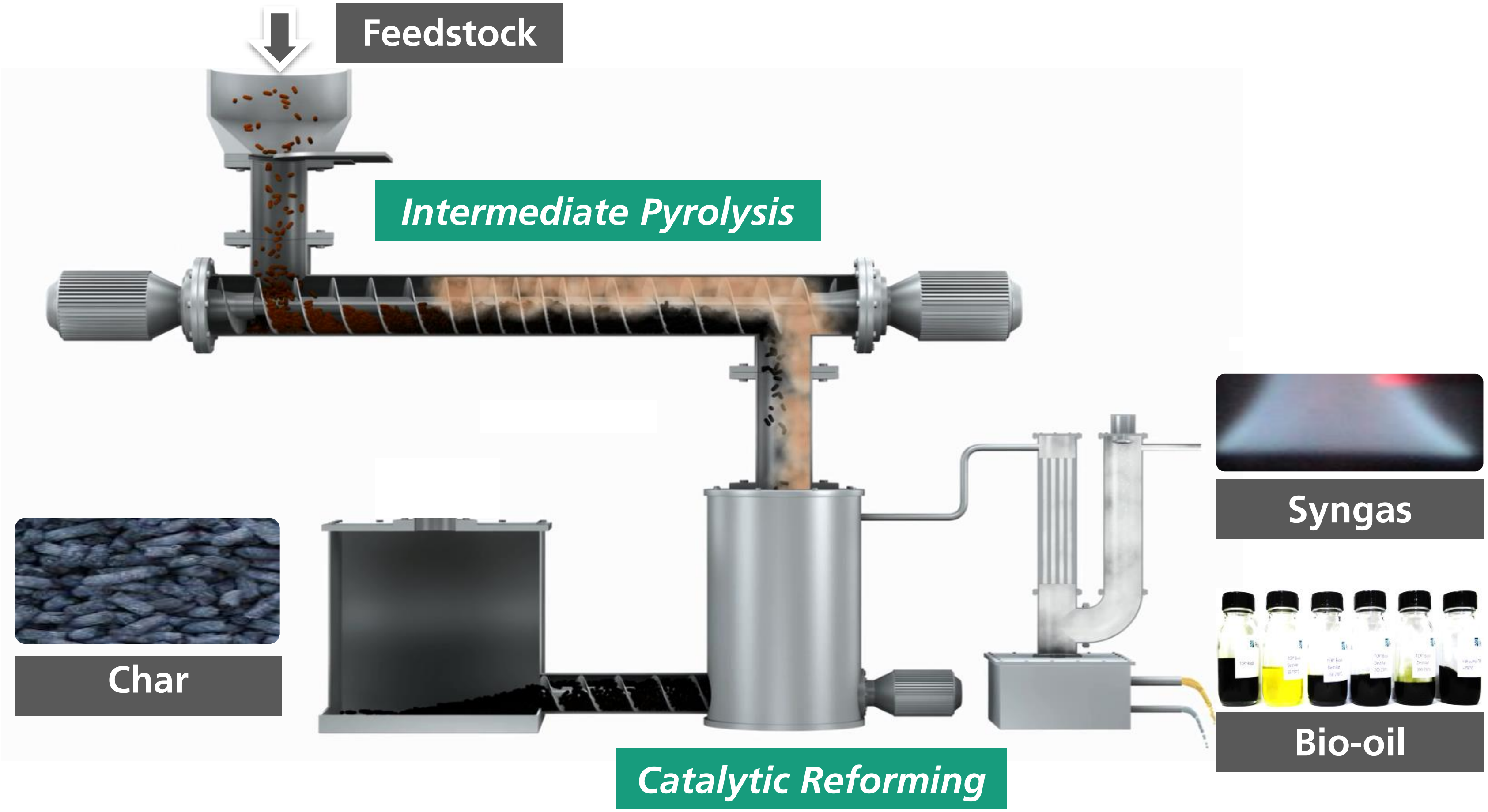
Pyroformer – Intermediate Pyrolysis and combined Reforming – Moderate heat transfer by char



Drying - Torrefaction - Pyrolysis Reforming - Char Conditioning

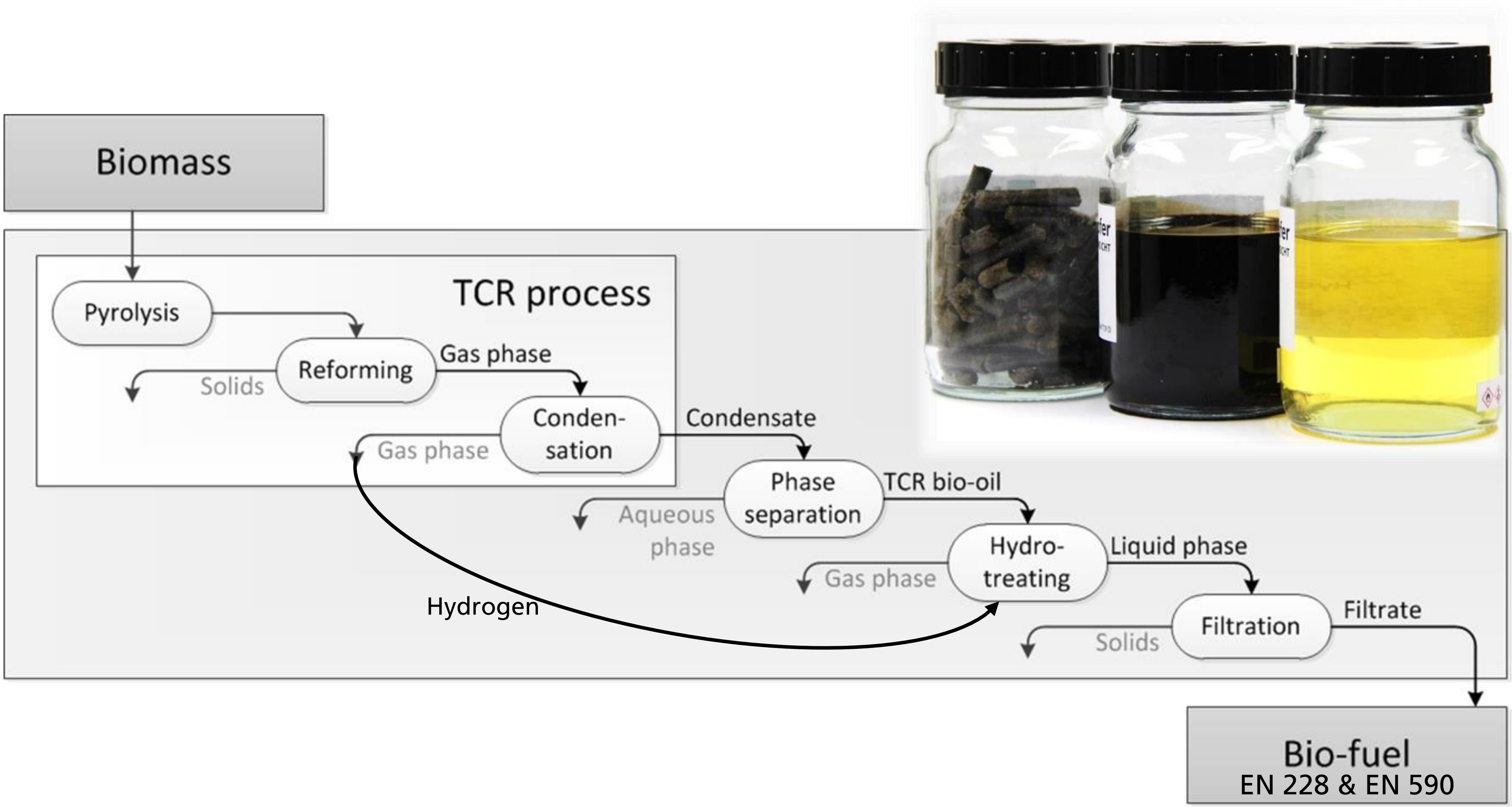
FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
UNIVERSITY OF BIRMINGHAM
ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA
Fraunhofer UMSICHT

Basement: Conversion of biomass
The Thermo-Catalytic Reforming (TCR®) technology

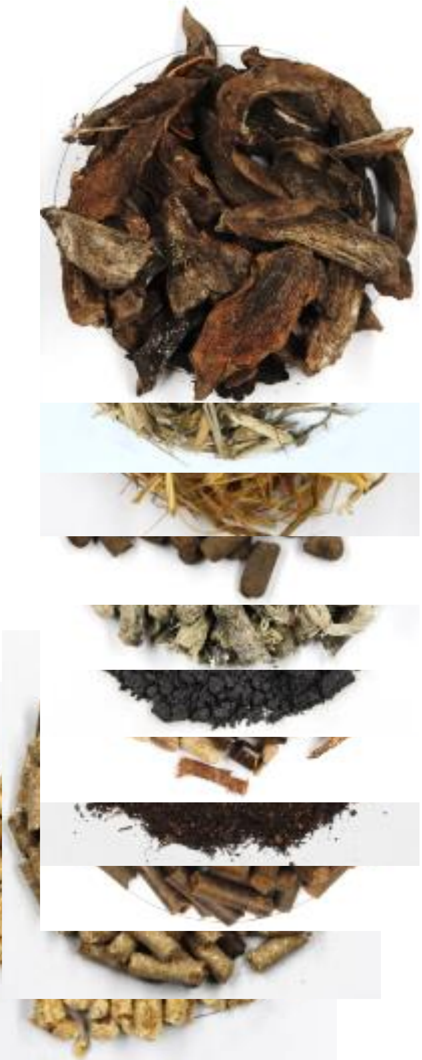


Fraunhofer
UMSICHT

From Biomass to Bio-chemicals or Bio-fuels
Overview



The Thermo-Catalytic Reforming technology
Process parameters



- Wide range of potential feedstocks
- Feedstock dry matter ~ 80% (optional pre-drying)
- Particle size > 2 mm
- Residence time 4-10 min
- Heating rate ~10 K/s
- Intermediate pyrolysis temperature ~450 °C
- Reformer temperature up to 750 °C

Fraunhofer UMSICHT

Thermo-Catalytic Reforming TCR®

Level of development: 2017

Scale Up x10

TCR300

Demonstration

Operational capacity: 300 kg/h

Heat Source: flue gas

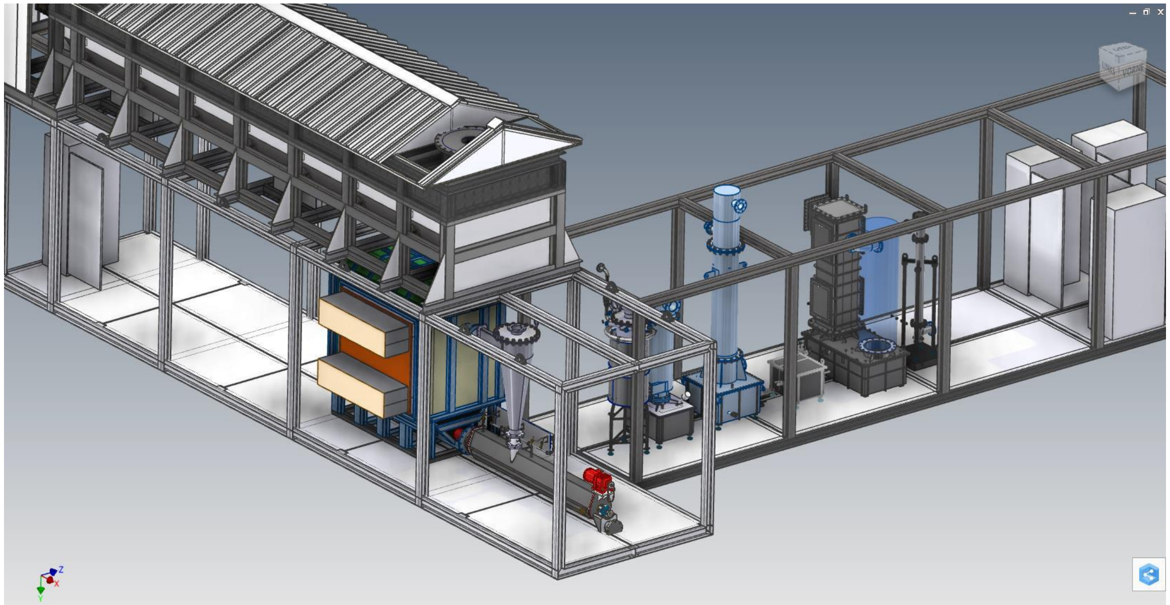
Purpose: scale-up, sludge treatment

Fraunhofer UMSICHT

Thermo-Catalytic Reforming TCR®

Level of development – today

Scale Up x2



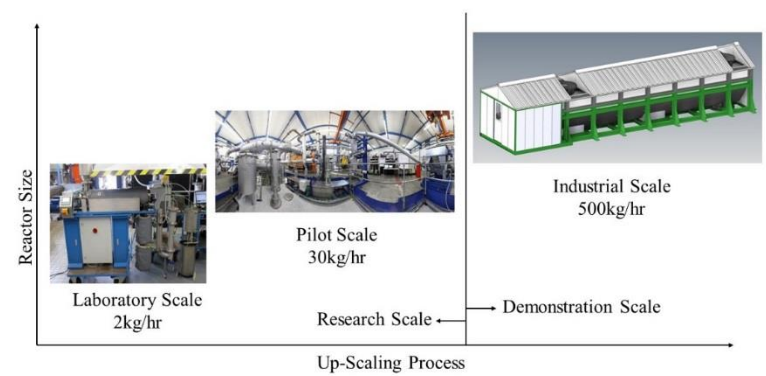
TCR500

Long-term demonstrator

Operational capacity: 500 kg/h

Heat Source: flue gas

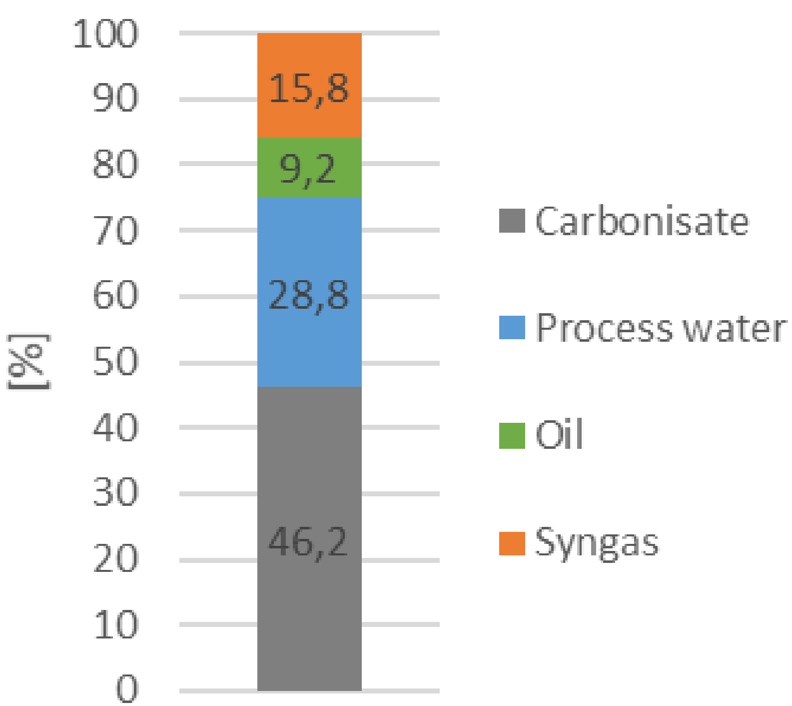
Purpose: pre-commercial demonstrator



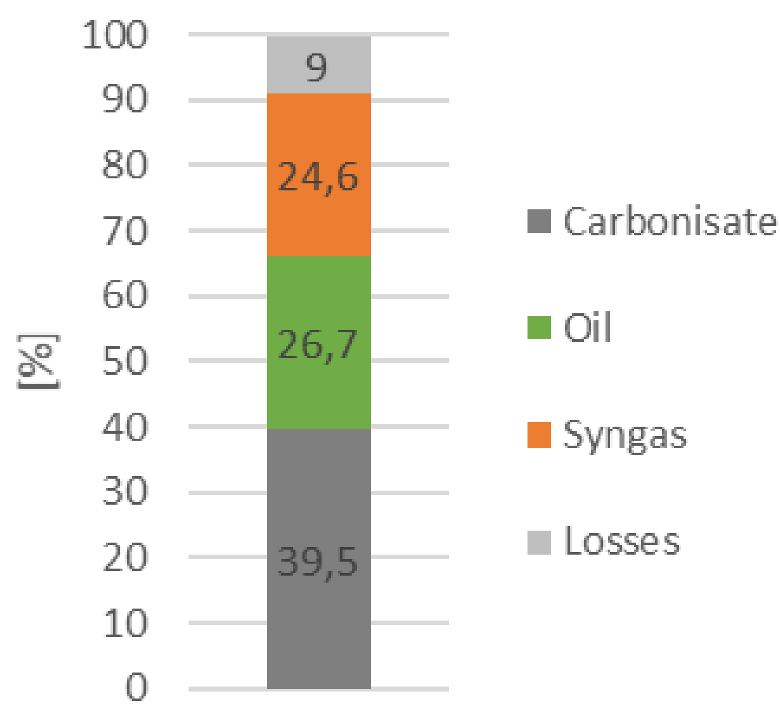
Up-Scaling of the TCR® Technology

Energy and mass balance for sewage sludge

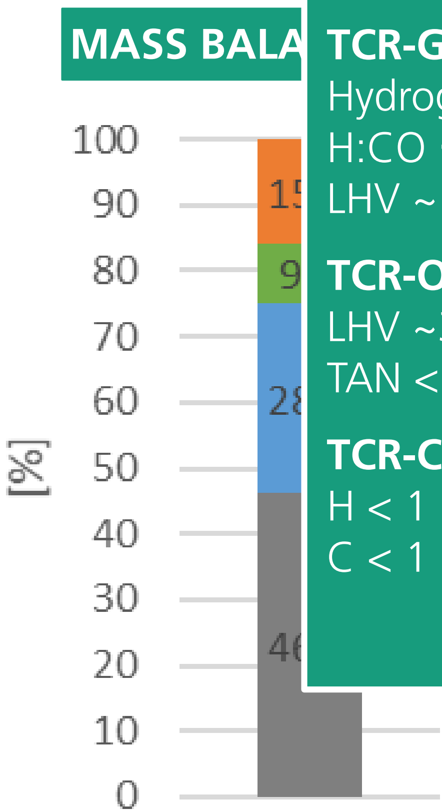
MASS BALANCE



ENERGY BALANCE



Up-Scaling of the TCR® Technology
Energy and mass balance for sewage sludge

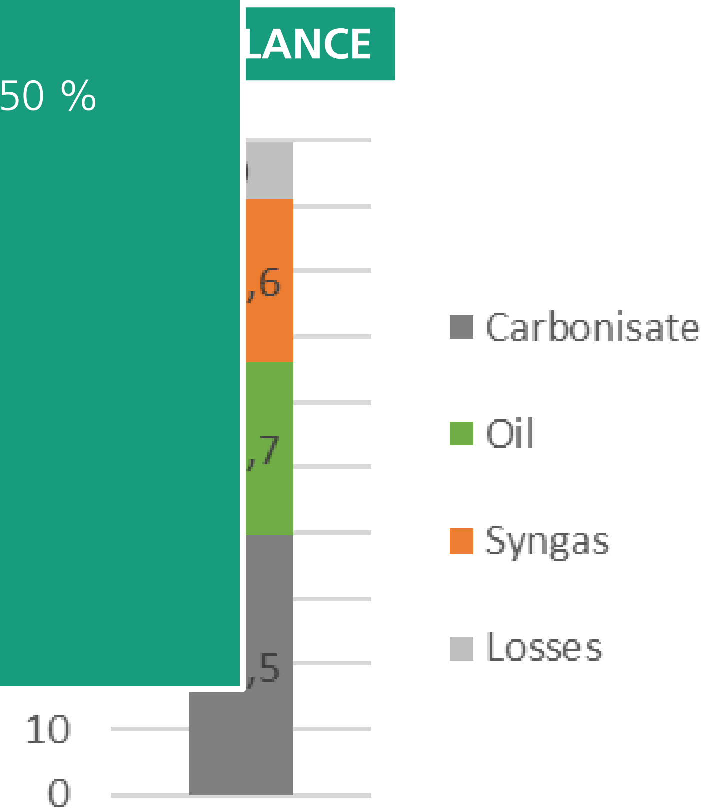


Results from TCR300-trials – highlights

TCR-Gas:
Hydrogen content ~30 Vol.-%, up to 50 %
H:CO → 3:1
LHV ~ 14 MJ/kg

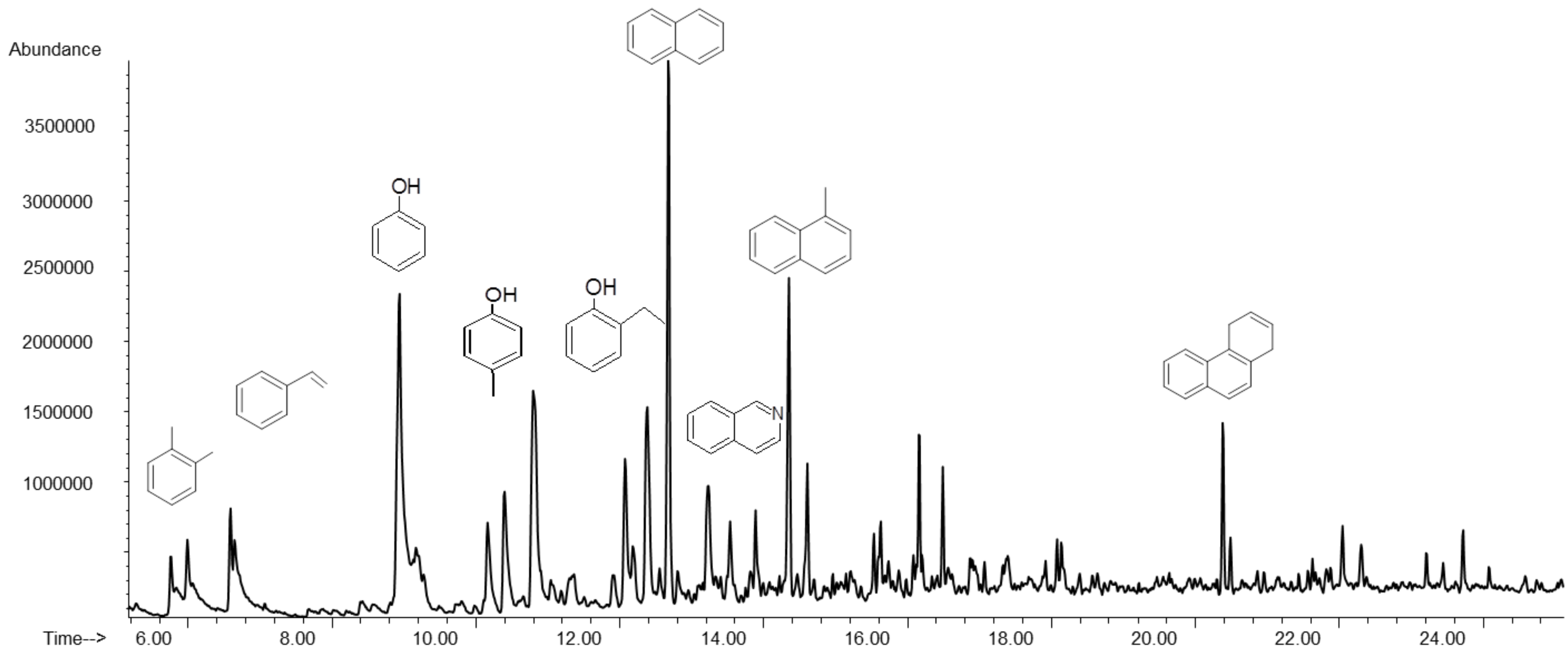
TCR-Oil:
LHV ~34 MJ/kg
TAN < 10 mgKOH/g

TCR-Carbonisate:
H < 1 Ma.-%
C < 1 Ma.-%



Fraunhofer UMSICHT

TCR®-Fuel
GC-MS analysis for TCR crude oil from digestate



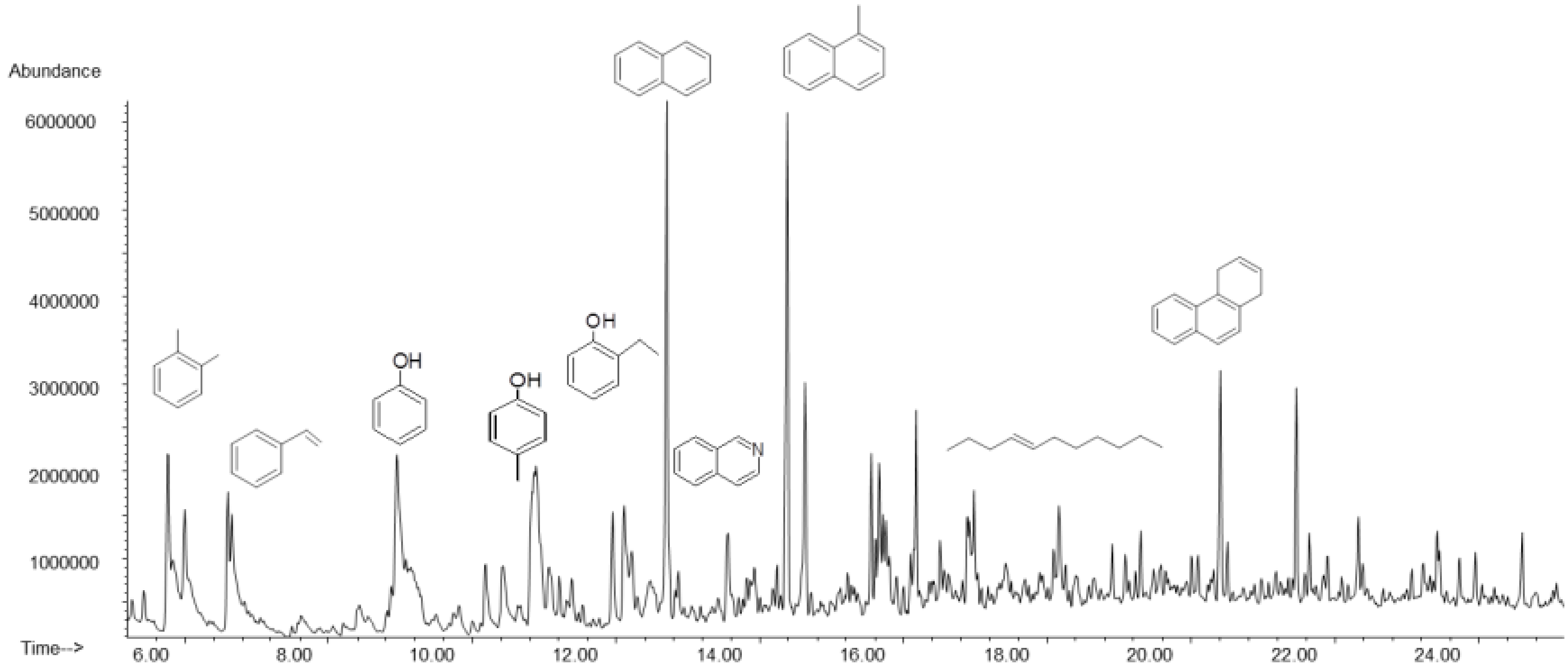
Aromatic Hydrocarbons: 28.7%

- Monoaromates (BTX): 9.2 %
- Polyaromates: 19.5 %

Phenole: 26.2%
N-components: 3.2%

TCR®-Fuel

GC-MS analysis for TCR crude oil from sewage sludge



Aromatic Hydrocarbons: 30.0%

- Monoaromates (BTX): 11.5 %
- Polyaromates: 18.5 %

Phenole: 12.1%
N-components: 1.8%

Fraunhofer UMSICHT

Comparison of the diesel fraction with EN 590

Diesel standard EN 590 min	max	Property	Unit	HDO TCR® diesel
51	-	Cetane Number		✓
46	-	Cetane Index		✓
820	845	Density at 15 °C	kg/m³	✓
-	8	PAH	% (m/m)	✓ 15 *
-	10	Sulfur	mg/kg	✓
55	-	Flash point	°C	✓
-	0,01	Ash content	% (m/m)	✓
-	200	Water content	mg/kg	✓
Class 1	Class 1	Copper strip corrosion (3 hours at 50 °C)	Class	✓
-	460	Lubricity at 60 °C	µm	✓
2	4,5	Viscosity at 40 °C	mm^2/s	✓
-20 (Winter)	0 (Summer)	CFPP	°C	✓
-	< 65	Volume at 250 °C	%V/V	✓
85	-	Volume at 350 °C	%V/V	✓
-	360	95 %(V/V) recovered at	°C	✓

* Achievable by an adjustment of the hydrotreating

Fraunhofer UMSICHT

Comparison of the gasoline fraction with EN 228

Gasoline standard EN 228 min	max	Property	Unit	HDO TCR® naphtha
720	775	Density	kg/m³	✓
-	5	Evaporation residue	mg/100ml	✓
-	35	Aromates	% (V/V)	✓
-	18	Benzene	% (V/V)	✓ 1.5*
-	1	Benzol	% (V/V)	✓
-	10	Sulfur	mg/kg	✓
-	5	Lead	mg/l	✓
-	2	Manganese	mg/l	✓
-	2,7	Oxygen	% (m/m)	✓ **
20	50	E70	% (V/V)	✓
46	71	E100	% (V/V)	✓
75	-	E150	% (V/V)	✓
-	210	End of Boiling Point	°C	✓
-	2	Distillation residue	% (V/V)	✓ **
45	90	Vapour pressure DVPE	kPa	✓

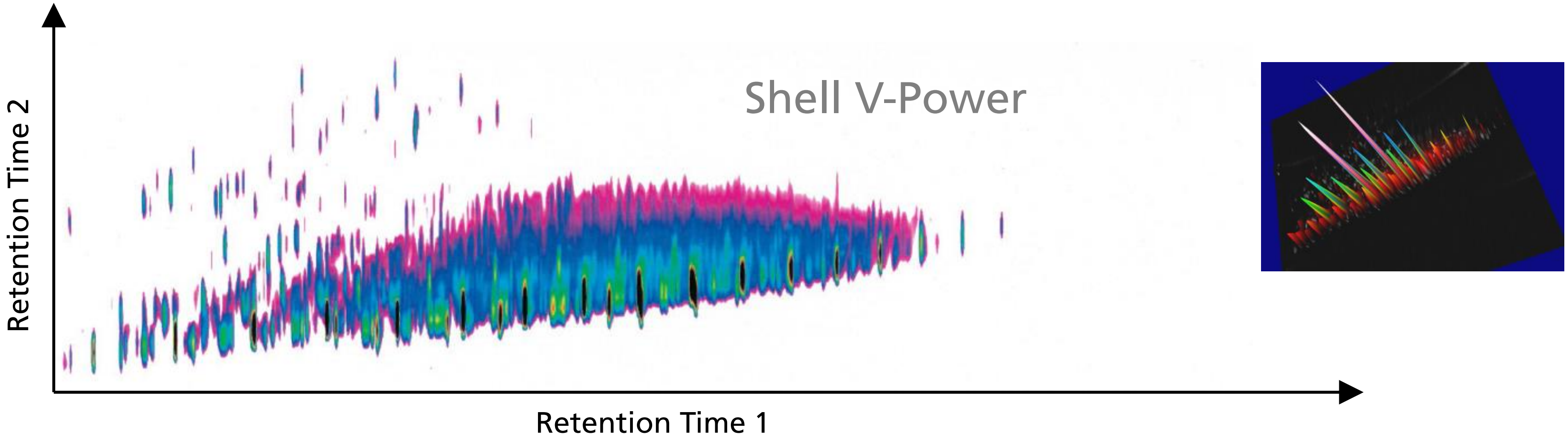
* Achievable by an adjustment of the hydrotreating

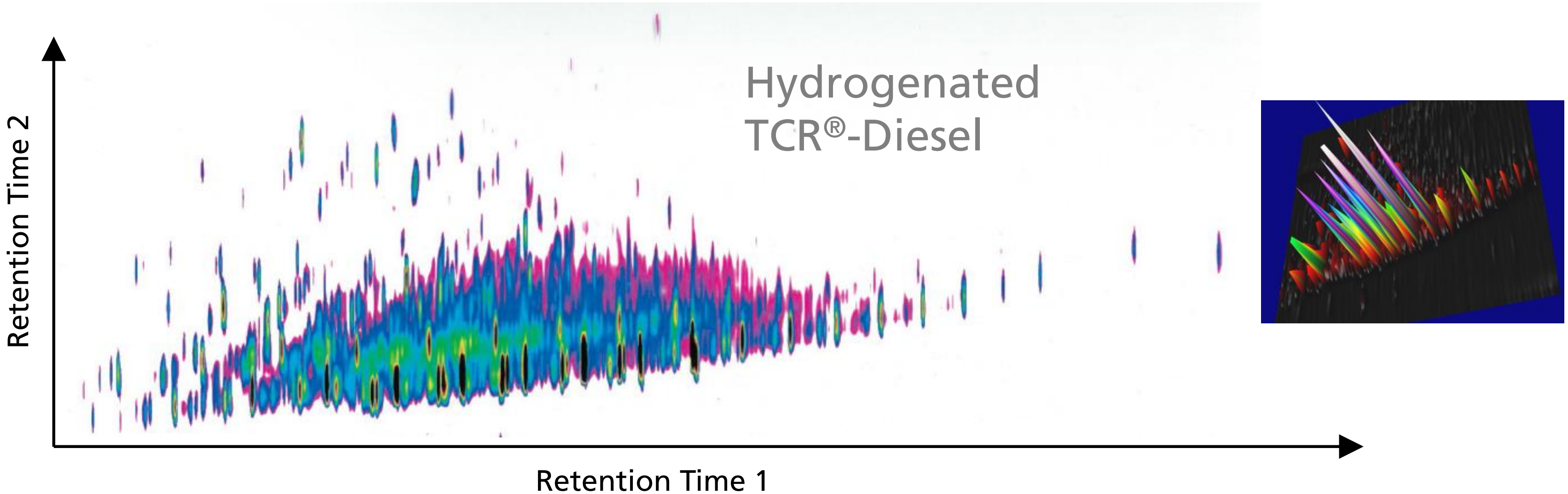
** Lack of light boilers due to laboratory distillation without cryocooler

Fraunhofer UMSICHT

TCR®-Fuel

Spectra of Diesel: Shell V-Power vs. TCR®-Diesel





Direct application of up to 30% TCR-oil made from sewage sludge in other fuels without modification of the engine of the car or a CHP system.

Direct application of TCR-diesel made from biomass without modification of the engine

Fraunhofer
UMSICHT

Product application
Pre-commercial demonstrator within ToSynFuel-project

Former rally world champion **Walter Röhrl** at ground breaking ceremony

Fraunhofer UMSICHT

Hydrogenation of TCR® Bio-oils from Sewage Sludge

TCR® BIO-OIL

C	76.6 wt%
H	9.0 wt%
N	7.3 wt%
S	1.6 wt%
O (diff.)	3.5 wt%
H_2O	2.0 wt%
Ash	< 0.005 wt%

LHV	34.8 MJ/kg
TAN	4.2 mg KOH/g
Viscosity	9,1 mm²/s
Density	960 kg/m³

HYDRIERUNG

HYDROGENATED TCR® BIO-OIL (HBO)

C	86.2 wt%
H	13.8 wt%
N	< 0.1 wt%
S	0.0015 wt%
O (diff.)	< 0.1 wt%
H_2O	0.0016 wt%
Ash	< 0.005 wt%

LHV	42.8 MJ/kg
TAN	< 0.1 mg KOH/g
Copper corr.	Grade 1
Flash point	< - 20 °C
Yield	~ 80 %

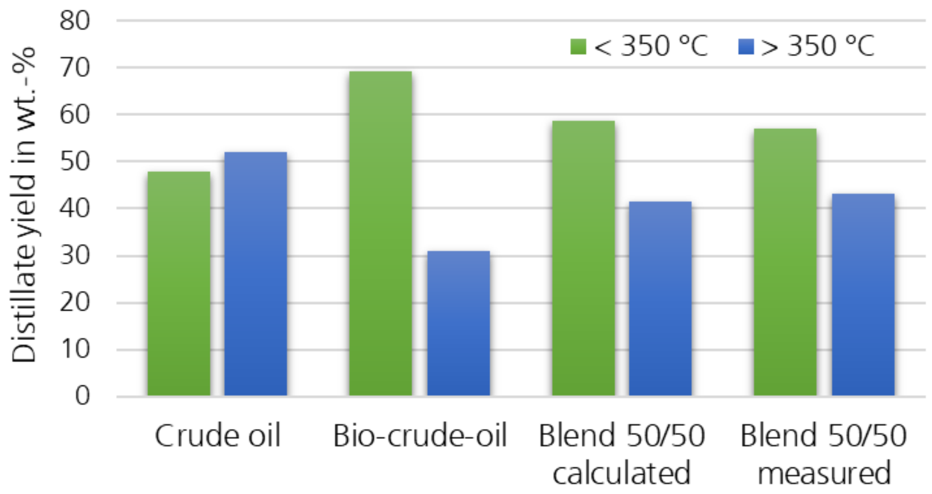
- Lab tests for Hydrotreatment at UMSICHT facilities
- Strategical partner VTS (Schwedt) for Hydrogenation

Fraunhofer UMSICHT

Sustainable transportation of fuels by co-processing of TCR®-bio-oil in conventional petroleum refineries

Distillation summary for crude oil and TCR®-bio-crude-oil

- More atmospheric distillable compounds in bio-oil than in the used crude oil
- Distillation results are comparable to calculated distributions (blend 50:50)
- Hydrotreatment removes 99.99 % of sulfur content
- No polymerization or coking during the upgrade

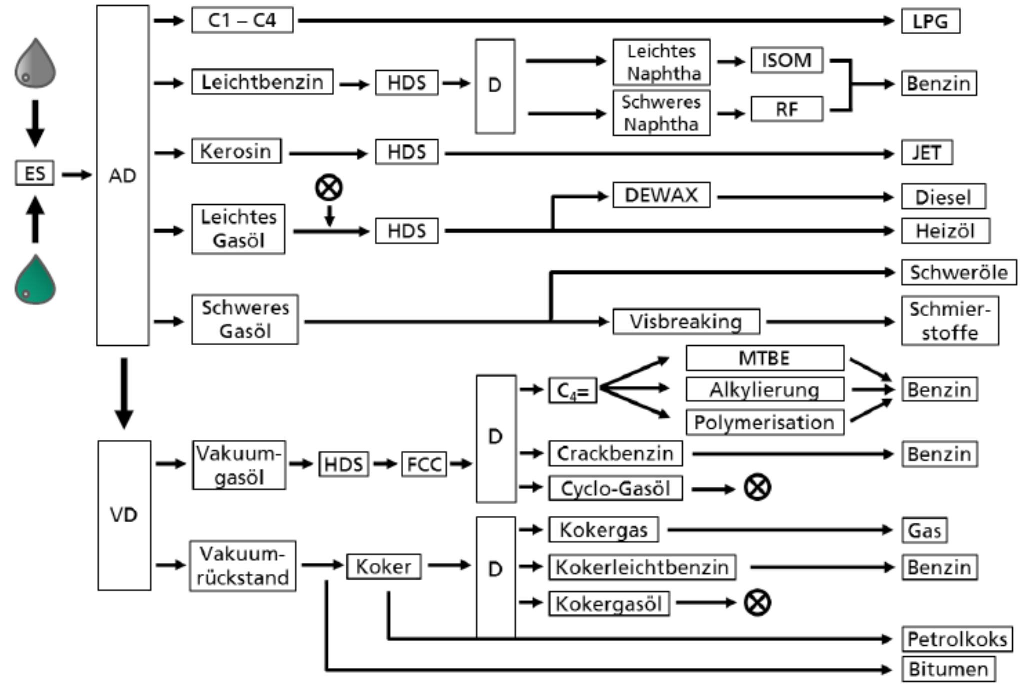


Green fuels from biomass residues and waste

Thermo-Catalytic Reforming technology – TCR®

Product utilization – Bio-Oil – Drop-in for Refineries

- TCR®-Oil is:
  - Thermal stable
  - Direct miscible with fossil crude oil
- Direct drop-in possible



Fraunhofer UMSICHT

Conclusion

- Crude TCR®-oil highlights
  - Thermally stable (atmospheric distillation)
  - Directly suitable for hydrotreating
  - Required hydrogen from TCR®-gas

- Hydrotreating highlights
  - Renewable chemicals extractable
  - Renewable gasoline (EN 228) and diesel (EN 590)
  - TCR® / Hydrotreatment demonstration at large scale within two EU-projects

Fraunhofer
UMSICHT

To-Syn-Fuel and FlexJet
Demonstration of Waste Biomass to Synthetic Fuels

Budget: 14,5 Mio. €

Partner: ENGIE, LEITAT Technological Center, University of Birmingham, eni, Susteen Technologies GmbH, GrantG, etaflorence, VTS, HYGEAR, SNB

FlexJet:
Sustainable Jet Fuel from Flexible Waste Biomass

Start: May 2018 (Horizon 2020)

13 partners

13,4 Mio. € (10 Mio. € funding)

Content: TCR®500 for the production of **1.200 tons green jet fuel**

Europäische Kommission

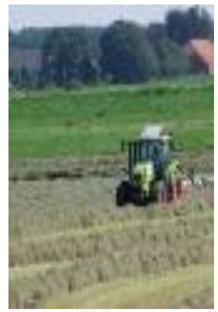
Fraunhofer UMSICHT

Recycling and Waste Management

TCR® und iCycle® – Technologies for Recycling & Energy Production

Biogenic Residues (TCR®)	Composites und Minerals (iCycle®)






Energy carrier from biomass & recycling of composites

Fraunhofer UMSICHT

Journal of Analytical and Applied Pyrolysis
46 (1998) 1–13

JOURNAL of ANALYTICAL and APPLIED PYROLYSIS

rgy Production

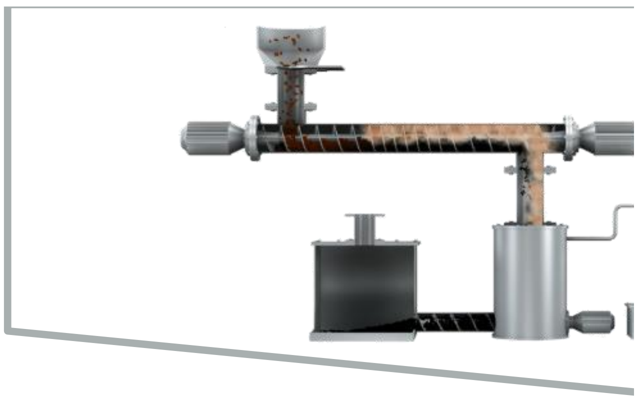
und Minerals (iCycle®)

Stepwise pyrolysis for raw material recovery from plastic waste

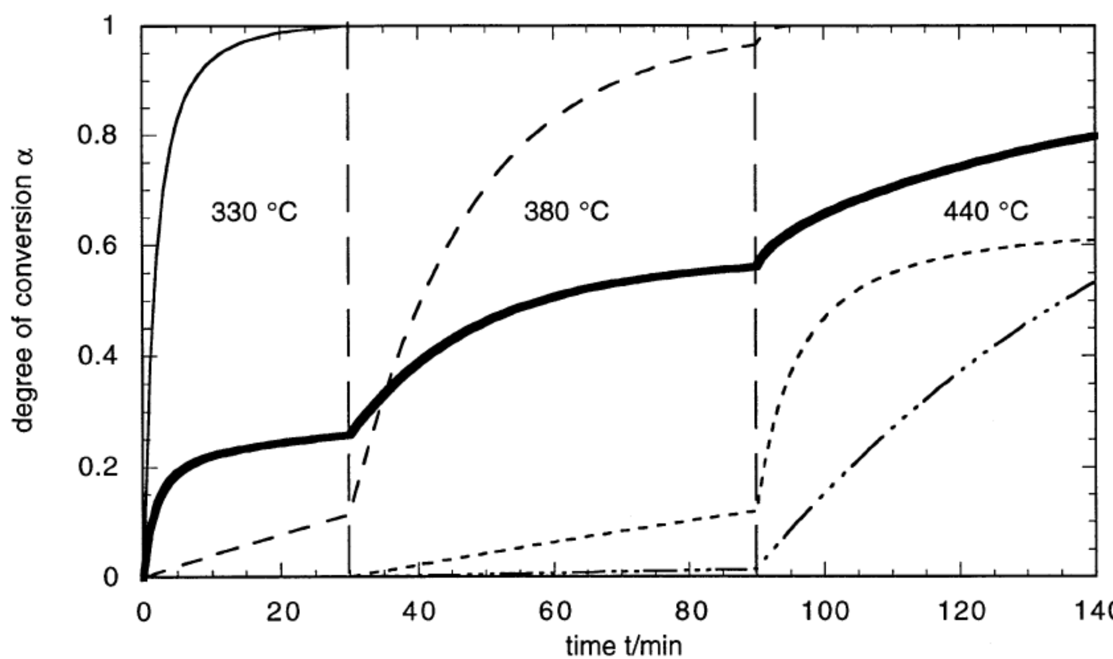
H. Bockhorn *, A. Hornung, U. Hornung

Institut für Chemische Technik, Universität Karlsruhe (TH), Kaiserstr. 12, 76128 Karlsruhe, Germany

Received 18 July 1997; accepted 17 February 1998



Energy carrier fr

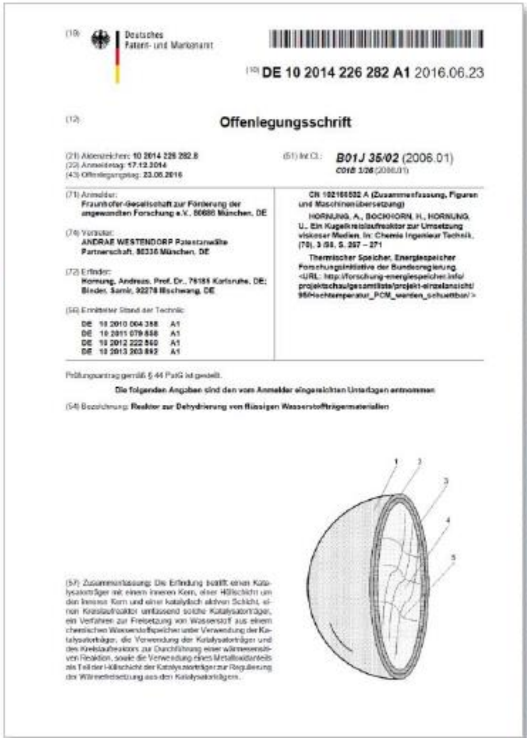


Feedstock recycling of polymers

Fraunhofer UMSICHT developments

Selective monomer recovery from complex waste plastic mixtures through stepwise degradation

- Important: reaction control and reactor design
- Fraunhofer UMSICHT designed and developed a special reactor (cycled-spheres reactor) and phase change materials
  - Both enable a selective initiation of c-c bond cracking in melting reactions



(19) Deutsches Patent- und Markenamt

(10) **DE 10 2014 226 282 A1** 2016.06.23

(12) **Offenlegungsschrift**

(21) Aktenzeichen: 10 2014 226 282.8
(22) Anmeldetag: 17.12.2014
(43) Offenlegungstag: 23.06.2016

(51) Int Cl.: *B01J 35/02* (2006.01)
C01B 3/26 (2006.01)

(71) Anmelder:
Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., 80686 München, DE

(74) Vertreter:
ANDRAE WESTENDORP Patentanwälte Partnerschaft, 80336 München, DE

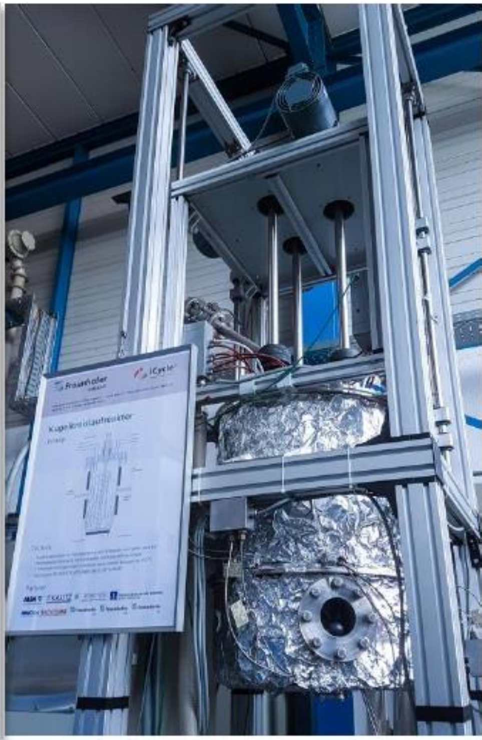
(72) Erfinder:
Hornung, Andreas, Prof. Dr., 76185 Karlsruhe, DE; Binder, Samir, 92278 Illschwang, DE

(56) Ermittelter Stand der Technik:
DE 10 2010 004 358 A1
DE 10 2011 079 858 A1
DE 10 2012 222 560 A1
DE 10 2013 203 892 A1
CN 102166532 A (Zusammenfassung, Figuren und Maschinenübersetzung)
HORNUNG, A., BOCKHORN, H., HORNUNG, U., Ein Kugelkreislaufreaktor zur Umsetzung viskoser Medien. In: Chemie Ingenieur Technik, (70), 3 /98, S. 267 – 271
Thermischer Speicher, Energiespeicher Forschungsinitiative der Bundesregierung. <URL: http://forschung-energiespeicher.info/projektschau/gesamtliste/projekt-einzelansicht/95/Hochtemperatur_PCM_werden_schuettbar/>

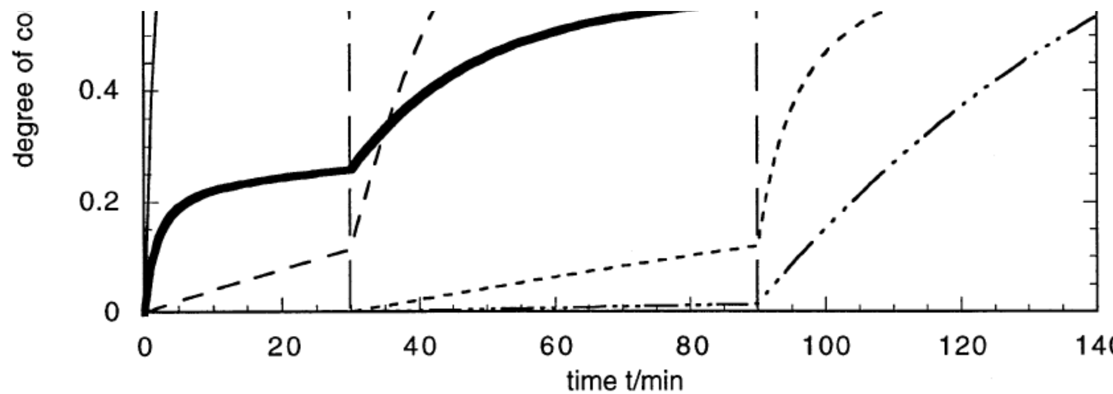
Prüfungsantrag gemäß § 44 PatG ist gestellt.

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: **Reaktor zur Dehydrierung von flüssigen Wasserstoffträgermaterialien**



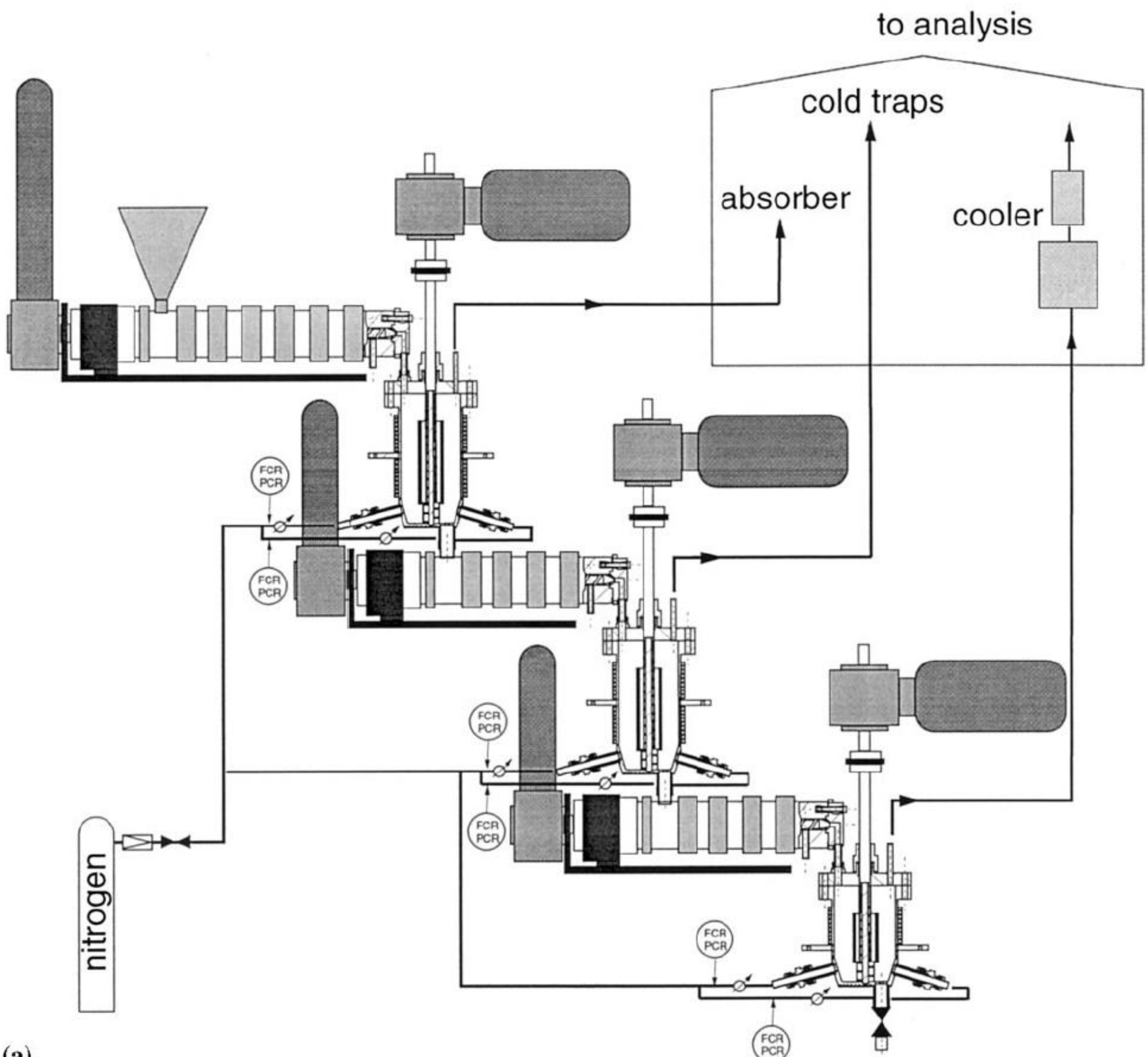
Energy carrier fr



Fe

Fra

Sele
plast

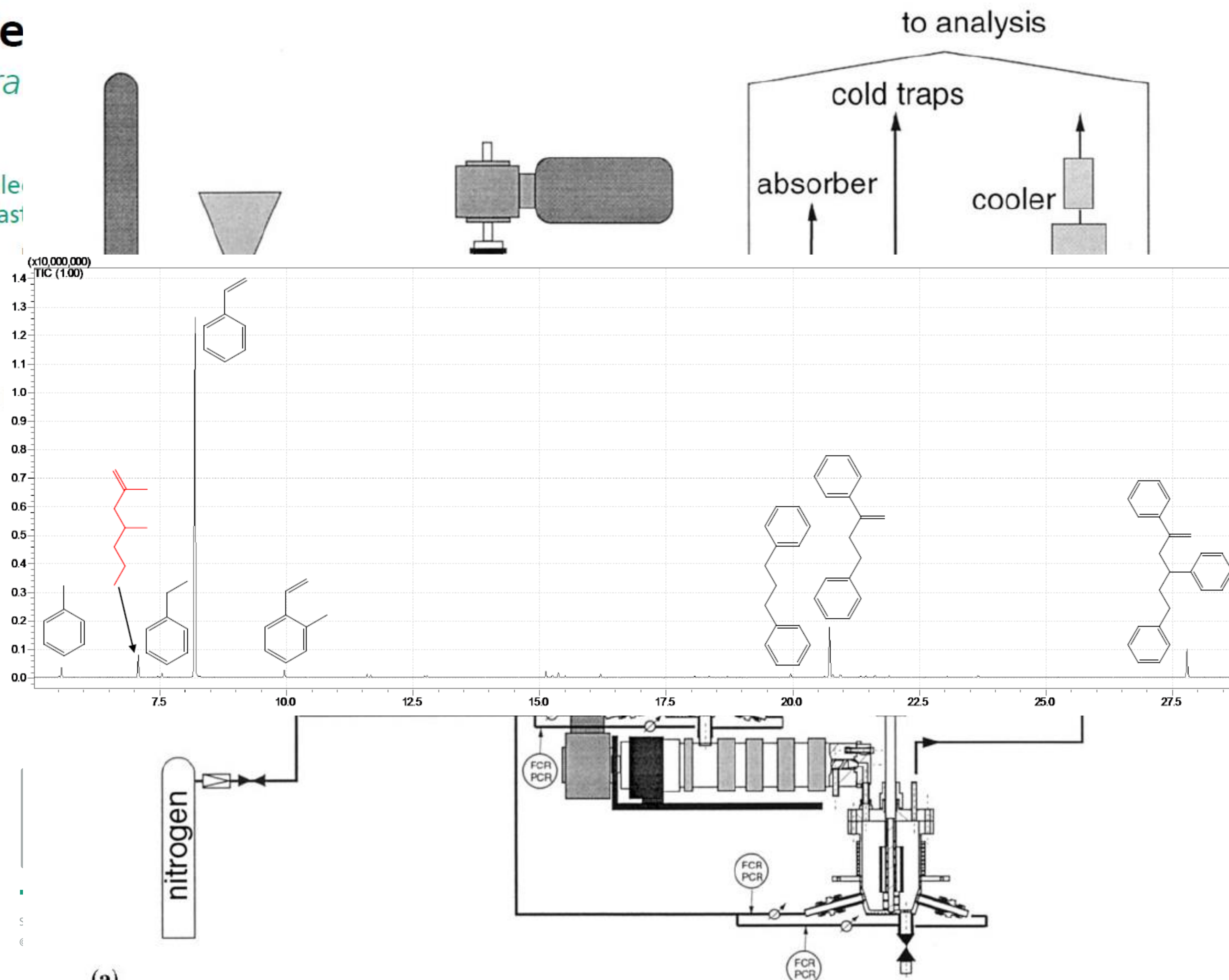


(a)

Fe

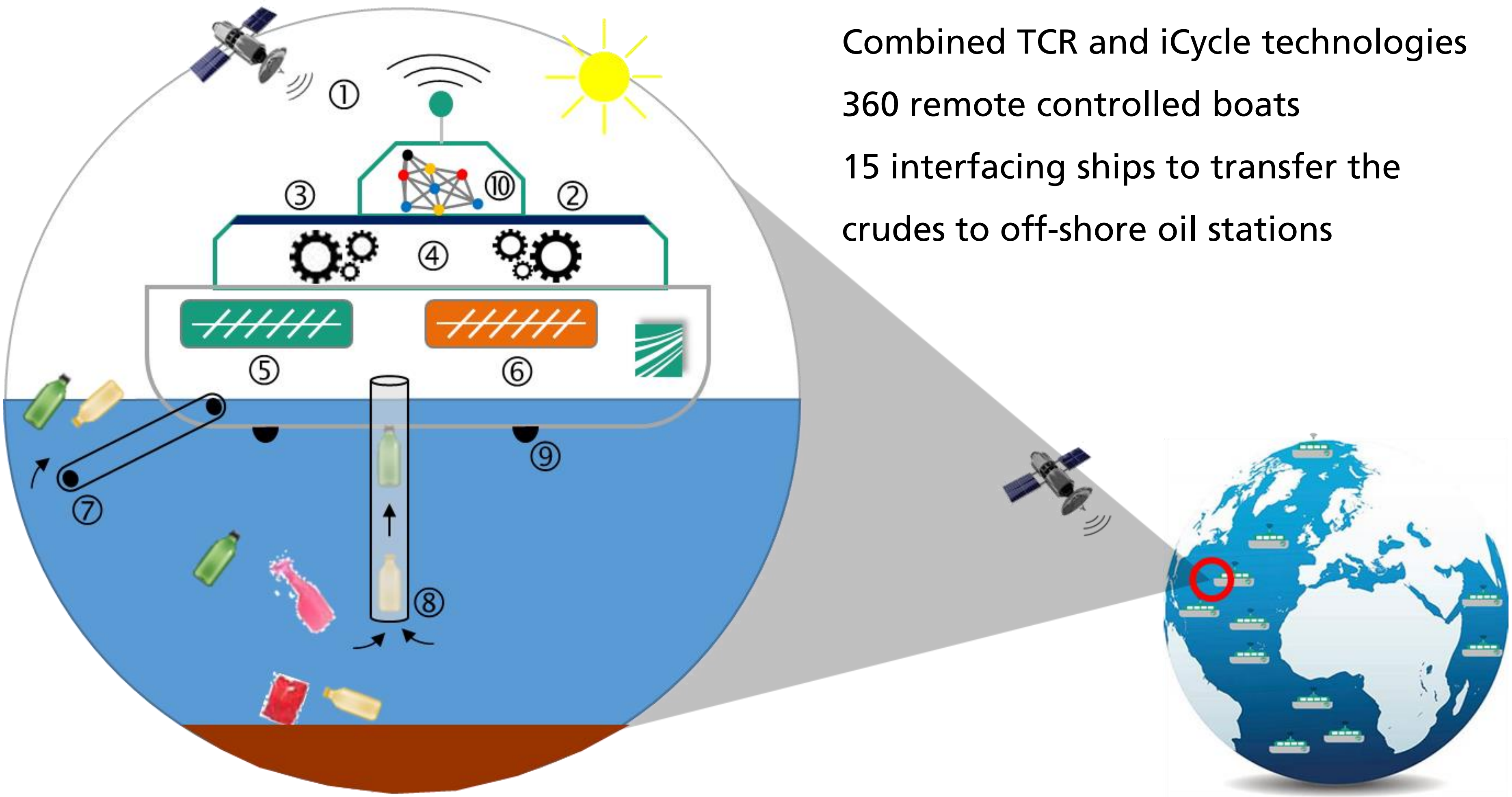
Fra

Sele
plast



(a)

SeaCycle by Fraunhofer Umsicht, to save the world climate and to protect the environment for future generations



Combined TCR and iCycle technologies

360 remote controlled boats

15 interfacing ships to transfer the crudes to off-shore oil stations

Fraunhofer UMSICHT

FEEDSTOCK – „The sleeping beauty“

Punjab region burns more than 20 Mt of biomass a year

The Hinterland in Brasil offers more than 300 Mt of biomass rotting every year.

Canadian forest are dying from beetles attack – Mt of dry matter per year

Sewage is available all over the world usually close to mankind. Allmost 10 Mt/a dry matter are reached in China

Up to 14 billion dry tonnes of macro algae can be made available world wide

Fraunhofer
UMSICHT

Conclusion – via intermediate pyrolysis/reforming it is possible to

produce green crude for refineries, getting to fuels and jet fuel

naphtha via refineries for chemical industry

produce three times the amount of crude as used today for plastic production in cultivation of macro algae (up to 14 billion dry matter)

close the phosphate cycle via gasification of anthracitic biochar

create a new sustainable end of life route - Converting green plastics into green fuels

Team in Sulzbach-Rosenberg

EN-Fuels from solid waste biomass by thermo-catalytic reforming

Contact
Fraunhofer UMSICHT, Fraunhofer Institute for Environmental, Safety, and Energy Technology
An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany
http://www.umsicht-suro.fraunhofer.de

Prof. Dr. rer. nat. Univ.- Prof. Dipl.-Ing. Andreas Hornung CEng FIChemE FRSC
E-Mail: andreas.hornung@umsicht.fraunhofer.de

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
UNIVERSITY OF BIRMINGHAM

Fraunhofer UMSICHT