SYNOVA

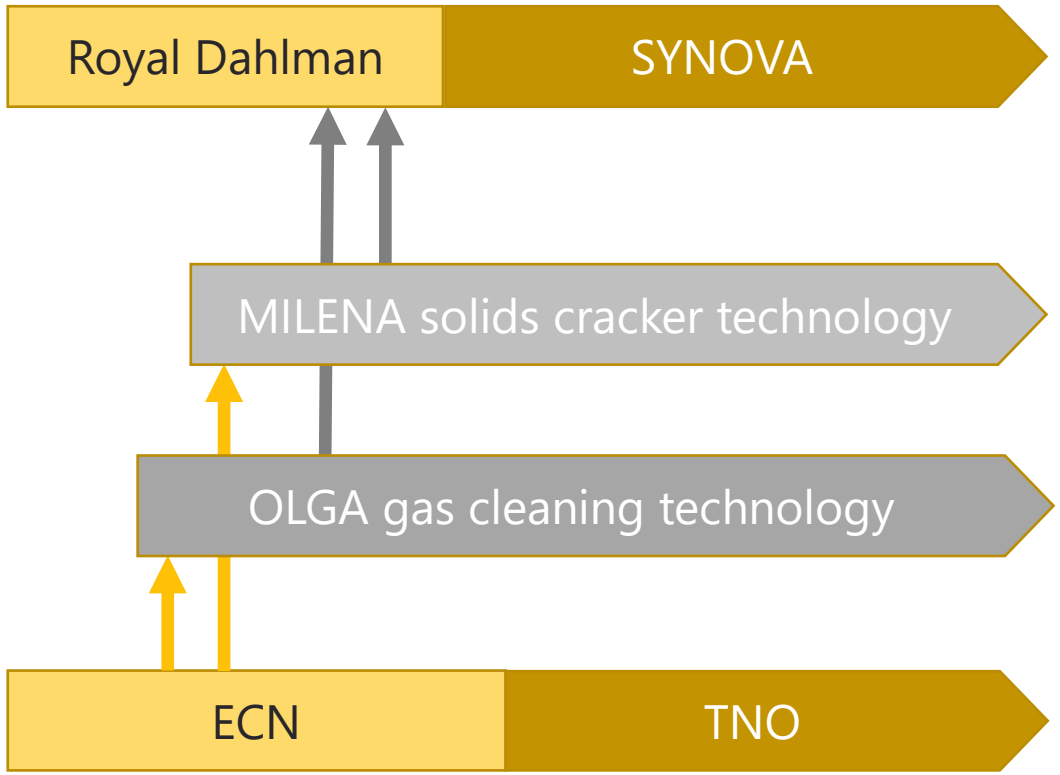
# Integrating waste cracking with existing petrochemical industry: the fate of contaminants

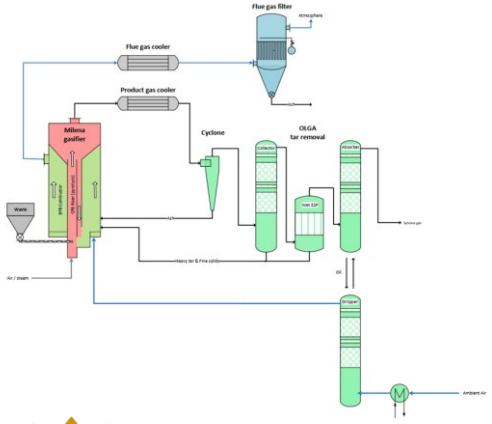
June 12th 2024

Robin Zwart

# WHO WE ARE

*A strong team providing defossilisation solutions*

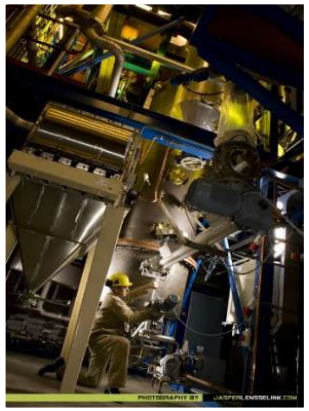



Technology and solutions development and commercialization

MOJI
milena olga joint innovation

Owns the IP



Research and development and feedstock testing

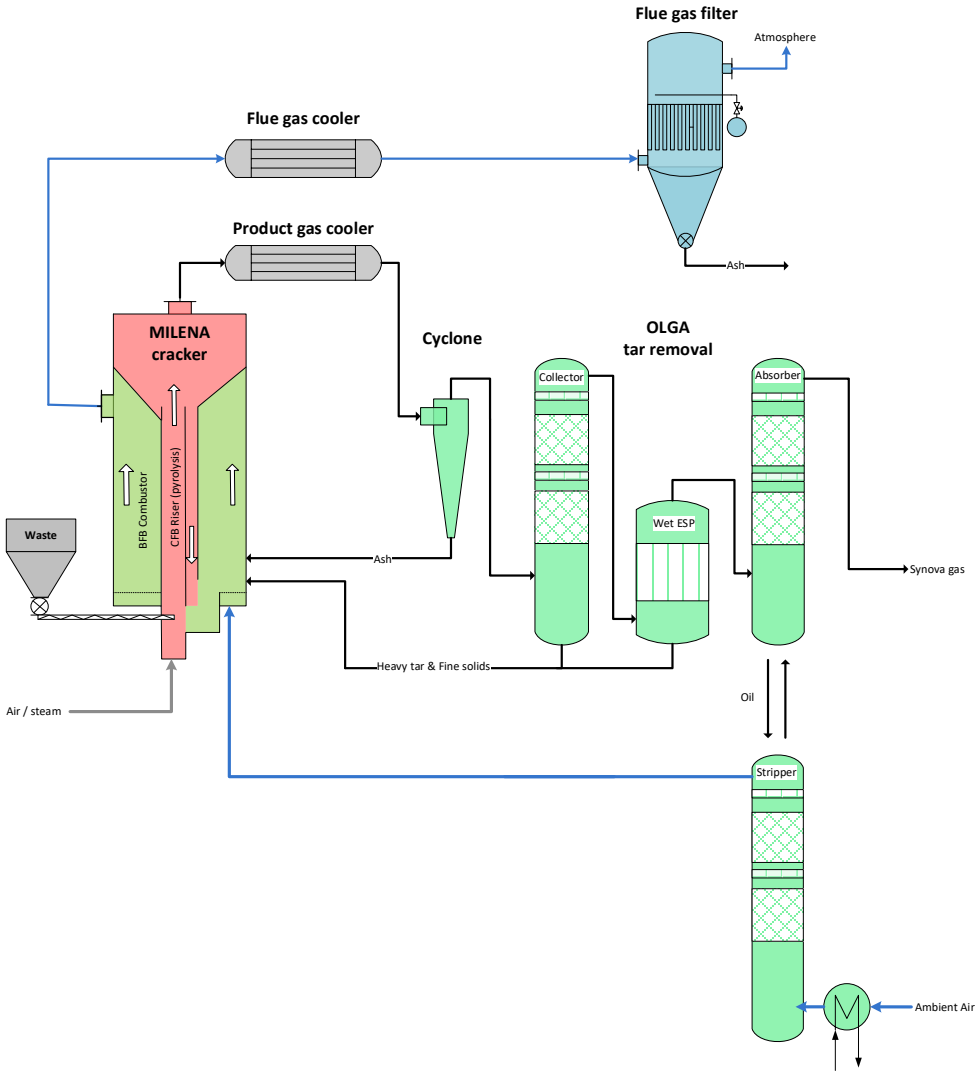
# WHAT WE DO

Developing and licensing chemical recycling solutions that convert waste to high-value chemicals

Developing and licensing renewable fuels solutions that convert biomass to renewable fuels

# OUR TECHNOLOGIES

*Continues, scalable, and robust, developed over past decennium to a TRL-level ready for commercial demonstration*




## MILENA solids cracker / gasifier

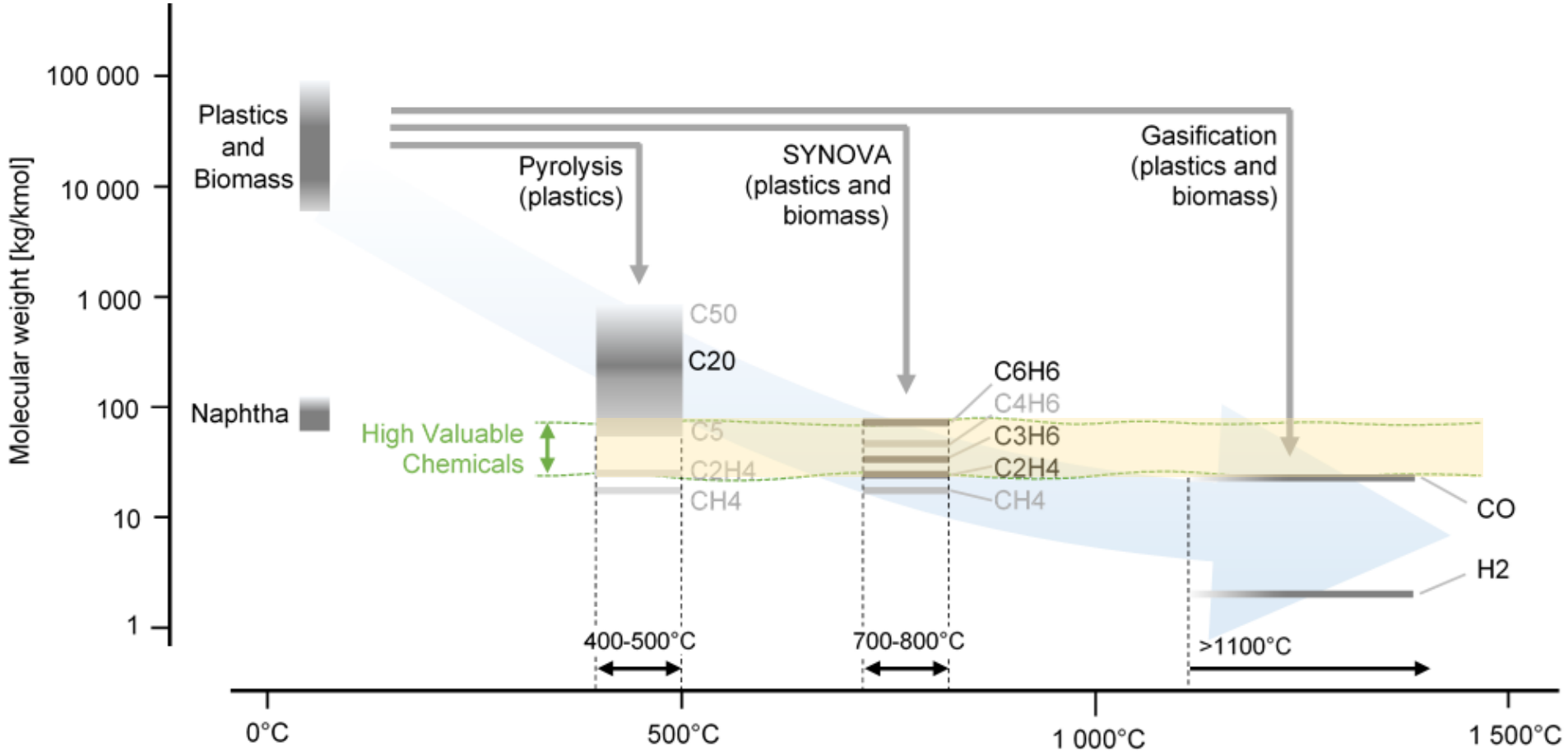
- MILENA technology based on FCC technology coupled fluidized beds
- Heat transfer via circulating sand, no catalyst
- Operating at ~750°C (depending on application and feedstock)
- No external fuels required (coke and heavies removed in OLGA or non condensable gas are combusted to provide the energy for cracking)

## OLGA tar removal

- OLGA technology based on Coke Oven Gas cleaning: gas/liquid contactors and Electrostatic Precipitator (ESP)
- Removes 99.9% of Poly Aromatic Hydrocarbons (heavies) and particles

# MEDIUM TEMPERATURE = INSTANT CHEMICALS

*Not too hot and not too cold, but just right…*



# OUR SOLUTIONS

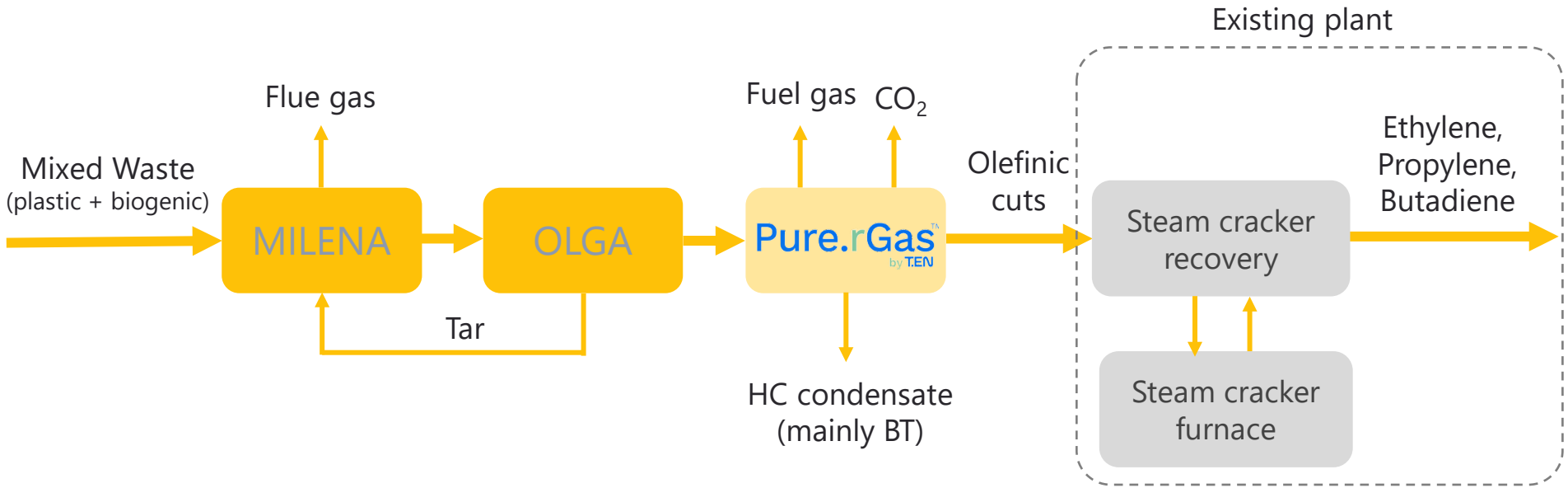
*Combining MILENA/OLGA with leading partner technologies*

| Application | Integration Options | Technology Partner | Announced Commercial Demonstration Partner |
|---|---|---|---|
| **Plastic-rich Waste to Olefins** | Downstream of steam cracker furnace | Technip Energies | SABIC |
| **Plastic-rich Waste to BTX** | Refinery or stand-alone | Koch Technology Solutions | Tba. |
| **Polystyrene-rich Waste to Styrene** | Existing Polystyrene plant or stand-alone | Trinseo | Trinseo |

Tests performed at TNO for several petrochemical industries on industrially sourced waste streams

# PROCESS FROM WASTE TO OLEFINS

*Integration of MILENA-OLGA with Pure.rGas™*



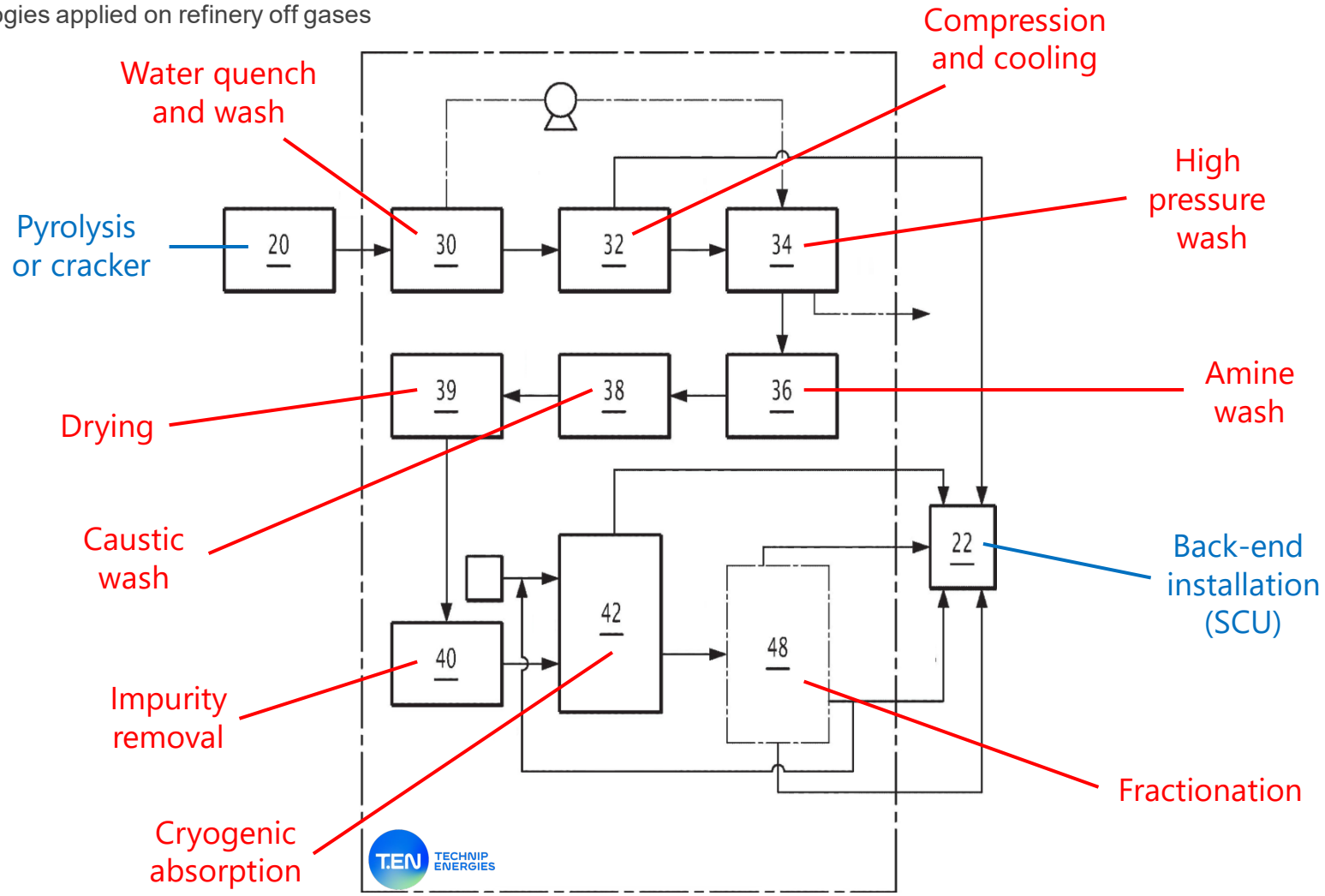

SYNOVA + T.EN TECHNIP ENERGIES

- Only one conversion step
- Integration with existing steam crackers by-passing the cracker furnace
- Possible with liquid and gas crackers
- Contaminants removed from the gas by Pure.rGas™

# PROCESS FROM WASTE TO OLEFINS

*General scheme of Pure.rGas™*

Based on technologies applied on refinery off gases




Reference: Veronique Reich, Yvon Simon and Walkiria Braga; Process for treating a gas stream from plastic pyrolysis and/or biomass pyrolysis and installation for integration into a steam cracker; US 2022/0402840 (2022)

# CONVENTIONAL FCC OFF GAS

*Typical impurities & their effect*

| Impurity | Effect |
|---|---|
| $H_2S$ | Catalyst poison |
| COS | Impacts on $C3^=$ product spec |
| RSH | Impacts on $C2^=/C3^=$ product spec |
| Acetylene | Impacts on $C2^=/C3^=$ product spec |
| Oxygen | Impacts on $C2^=/C3^=$ product spec |
| Chlorides | Corrosive to aluminum |
| Ammonia | Potential reactant to form $NH_4NO_3$ |
| Nitric oxides | Can react to form explosive nitroso gums |
| Mercury | Attacks aluminum in cold section |
| Arsine | Impacts on $C3^=$ product spec |
| HCN | Impacts on $C2^=/C3^=$ product spec |
| $H_2O$ | Freezes in cold section |

Reference: Gerard B Hawkins, FCC off gas treatment, GBH Enterprises, Ltd (2013)

# CONVENTIONAL FCC OFF GAS

*Typical impurities & their removal*

| Impurity | Removal |
|---|---|
| $H_2S$ | Amine/caustic wash + absorbent guard bed |
| COS | Hydrolysis or solid bed absorption |
| RSH | Caustic and/or solid bed absorption |
| Acetylene | Hydrogenation to ethylene across catalyst |
| Oxygen | Hydrogenation to water across catalyst |
| Chlorides | Solid bed absorbent |
| Ammonia | … |
| Nitric oxides | Hydrogenation to $NH_3$ across catalyst |
| Mercury | Solid bed absorbent |
| Arsine | Solid bed absorbent |
| HCN | Solid bed absorbent or hydrogenation across catalyst |
| $H_2O$ | Regenerable mol sieve |

Reference: Gerard B Hawkins, FCC off gas treatment, GBH Enterprises, Ltd (2013)

# CONTAMINANT TESTING

## *MILENA-OLGA operated on industrial sourced DKR-350*

Industrial MILENA handles the original shredded waste, fuel pretreatment with pelletization and milling is needed only as of size of the PDU




Of all plastic in your blue/ orange/yellow bag one third ends up in DKR-350 that has little/ to no market and is often incinerated.

That is roughly a similar fraction as plastics that go to recycling (the purpose of introducing the b/o/y bag).

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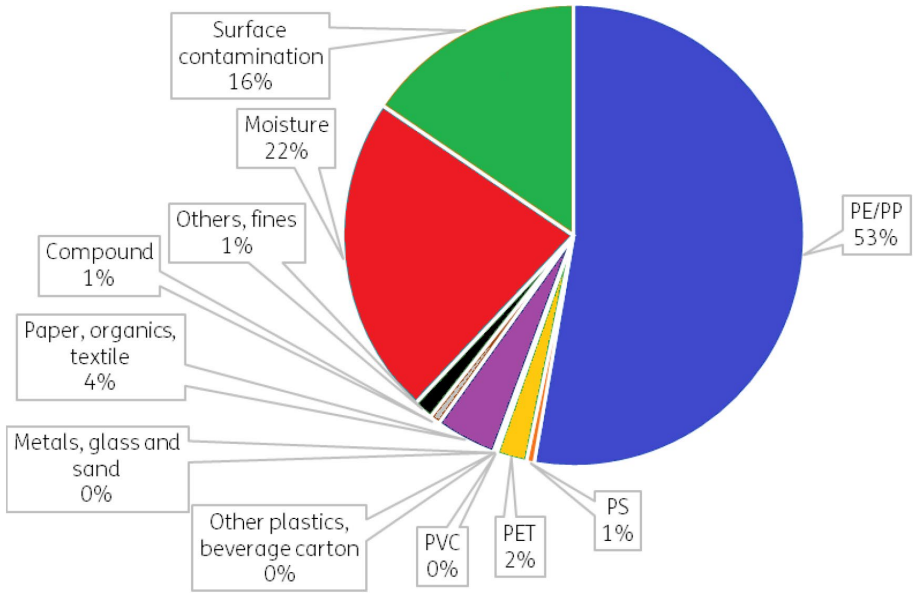
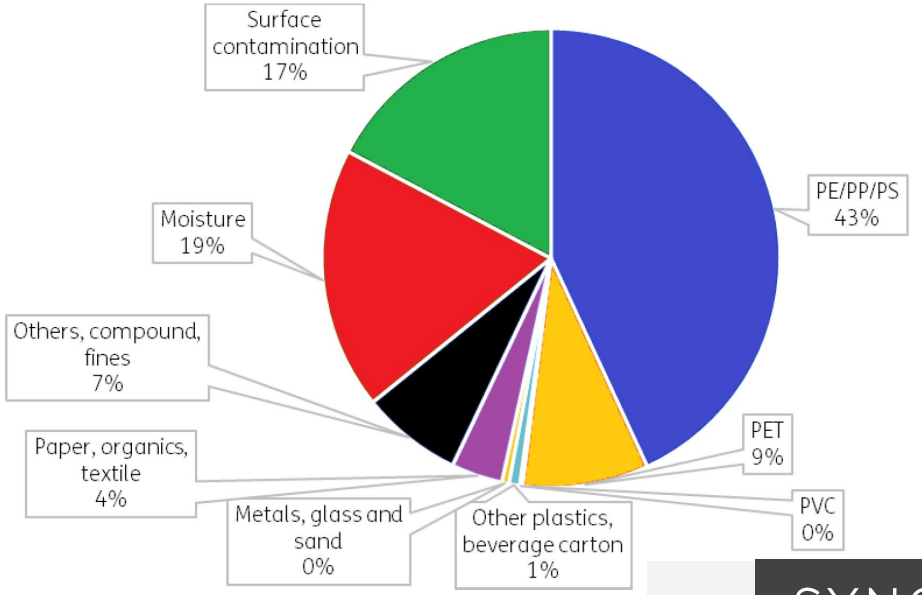
Composition pie charts are based on visual inspection and sorting. Composition based Carbon-14 and ultimate analyses show more biogenic content.



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# CONTAMINANT TESTING

## *MILENA-OLGA operated on industrial sourced DKR-350*

Industrial MILENA handles the original shredded waste, fuel pretreatment with pelletization and milling is needed only as of size of the PDU

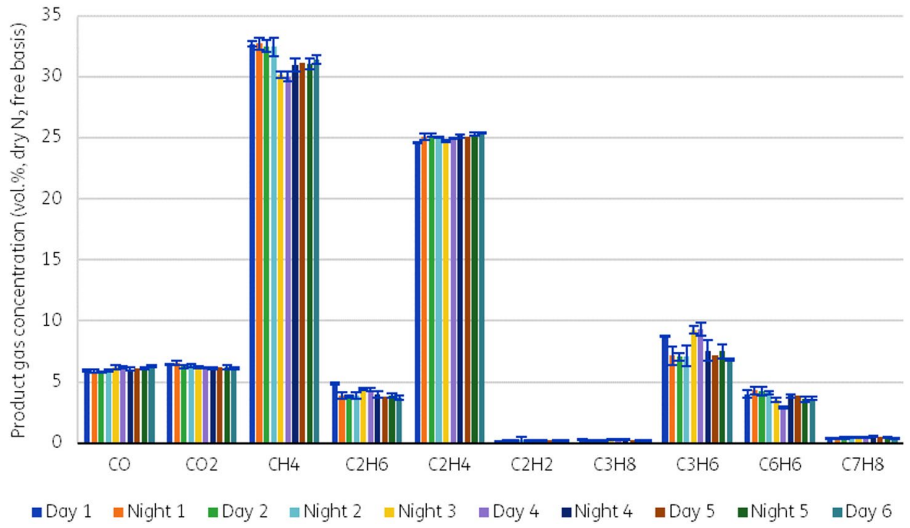


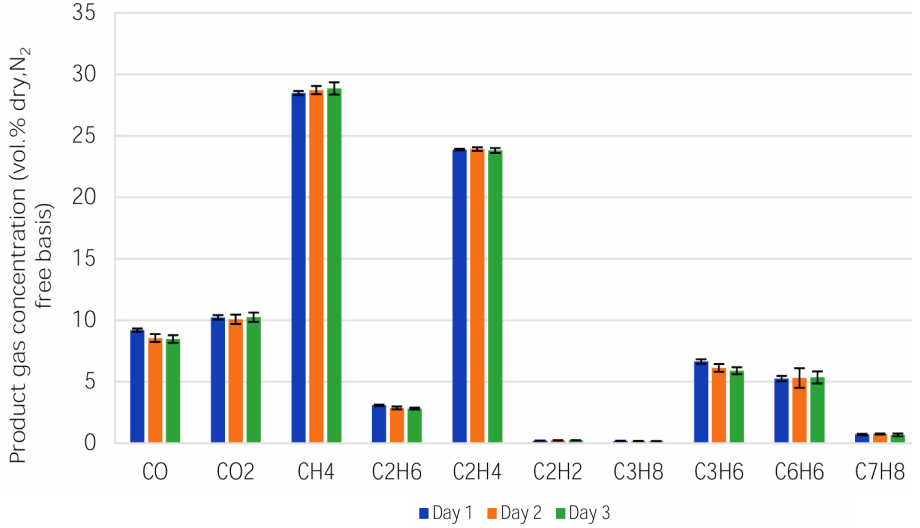

Over 40 vol.% of the gas are $C2^+$ components (dry and $N_2$ free basis).

50 kta mixed waste will generate 13.5 kta ethylene and propylene, or 19 kta of high value chemicals.

Mixed waste being 59% mixed plastics and 29% biomass (other water/inert).

Total ethylene/propylene equals 45 wt.% as of % of plastic processed.



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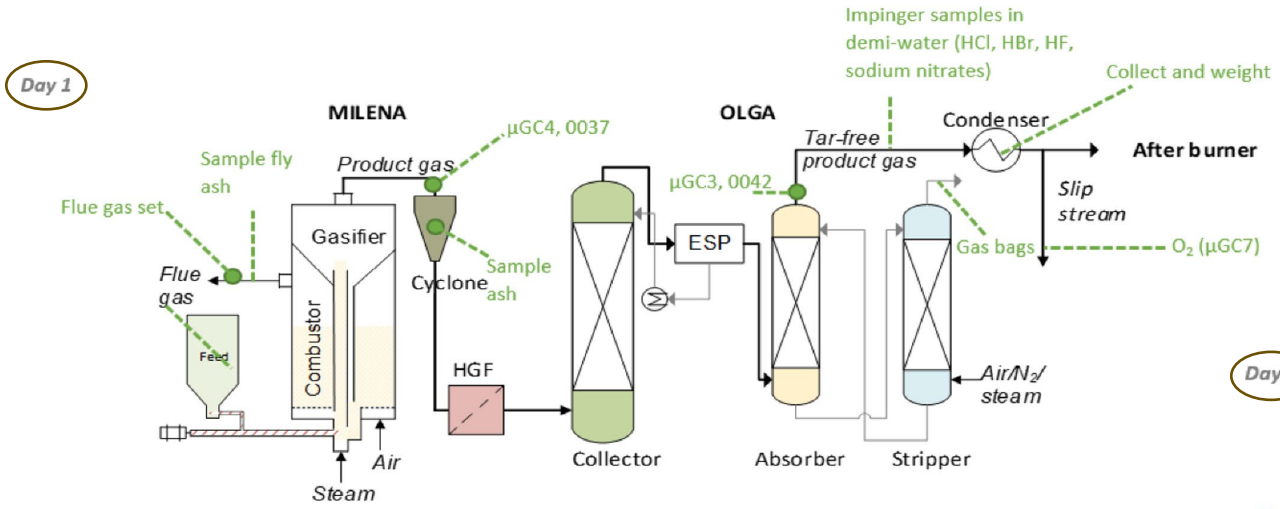
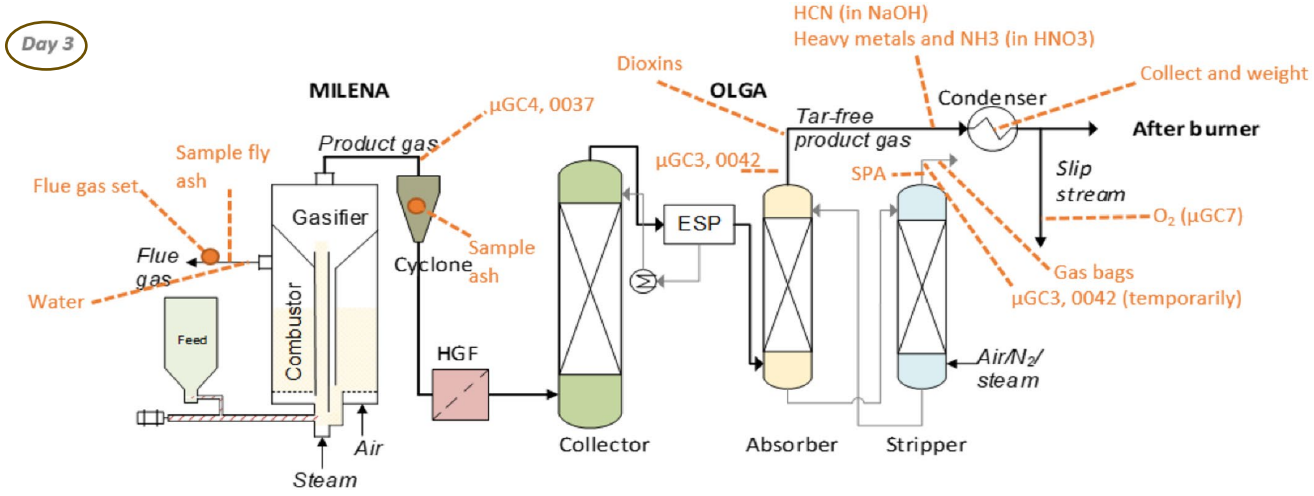
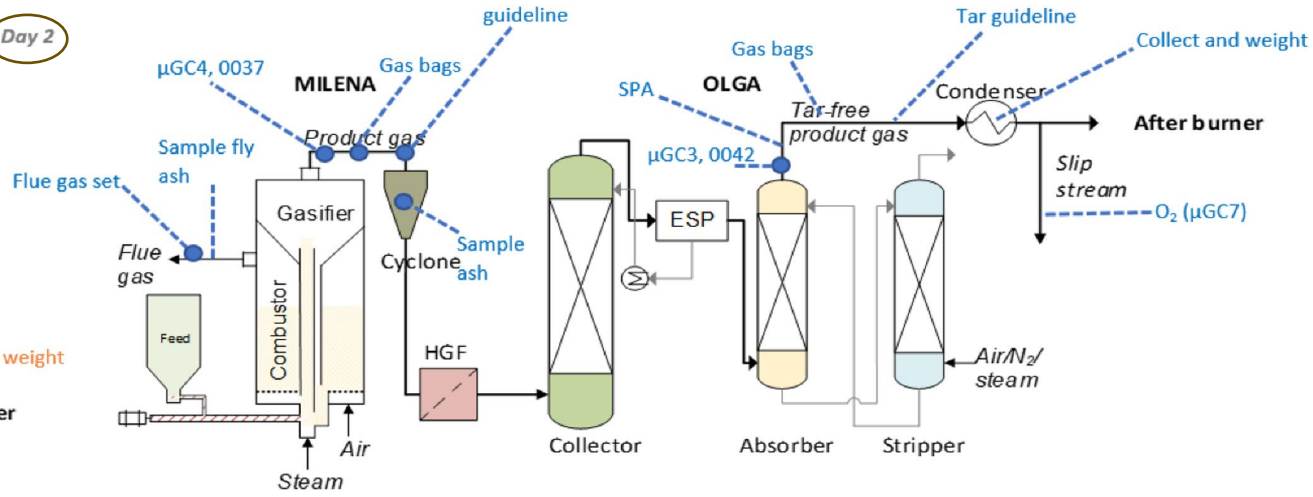
# CONTAMINANT TESTING

*Contaminant testing primarily focusing on product gas*






SYNOVA

# MILENA-OLGA PRODUCT GAS

*Additional concerns raised as of differences in feedstock*

| Impurity | Effect |
|---|---|
| $H_2$, CO, $CO_2$ and $H_2O$ | Disturbance of SCU as of high quantities |
| Aromatic hydrocarbons (tars) | Promote fouling and pollute pygas product |
| $H_2S$, COS, mercaptans and thiophenes | Pollute final products and/or hydrogenation catalyst |
| $NH_3$ and HCN | Pollute ethylene product and impact catalyst |
| HCl, $Cl_2$ and organic chlorides | Corrosion risk, catalyst poison and pollute final products |
| Acetates and aldehydes | Promote fouling and poison catalysts |
| Acids (including fatty) | Promote fouling and poison catalysts |
| Alcohols, diols and ketones | Promote fouling and poison catalysts |
| Dioxins and PFAS | Contaminate product and form environmental problem |
| Esters and ethers | Promote fouling and poison catalysts |
| Silicones | Permanent poison of catalyst and pollute pygas product |
| Oxygen and nitric oxides | Safety issue related to explosion risk |

Feedstock: Industrially sorted DKR-350 with biogenic fraction as well as PET and other plastics (everything not being naphtha)

# MILENA-OLGA PRODUCT GAS

*Analysed levels for different contaminant & laboratories included*

| Impurity | Levels | Laboratories |
|---|---|---|
| $H_2$, CO, $CO_2$ and $H_2O$ | vol.% | TNO innovation for life |
| Aromatic hydrocarbons (tars) | $mg/Nm^3$ | سابك sabic |
| $H_2S$, COS, mercaptans and thiophenes | ppmv | |
| $NH_3$ and HCN | ppmv | |
| HCl, $Cl_2$ and organic chlorides | ppmv | intertek Total Quality. Assured. |
| Acetates and aldehydes | ppmv | |
| Acids (including fatty) | ppmv | SGS |
| Alcohols, diols and ketones | ppmv | |
| Dioxins and PFAS | $ng/Nm^3$ | BUREAU VERITAS 1828 |
| Esters and ethers | ppmv | |
| Silicones | ppmv | |
| Oxygen and nitric oxides | ppmv and ppbv | |

# CONCLUSIONS

- Contaminant testing was done with the PDU at TNO on two DKR-350 waste streams in two times three days with operation in daytime.
- Steady state conditions in terms of flow, temperature and product gas composition could be established for all three days and were also comparable with one another.
- For the analyses of $200^{+}$ contaminants, not only available analytical capabilities of TNO were applied, but also those of the external laboratories of SABIC, Intertek, SGS and Bureau Veritas.
- Measured levels for contaminants have been used in validating OLGA and Pure.rGas™ abilities to remove contaminants to within the required specifications for steam cracker integration.

# Thank you!

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