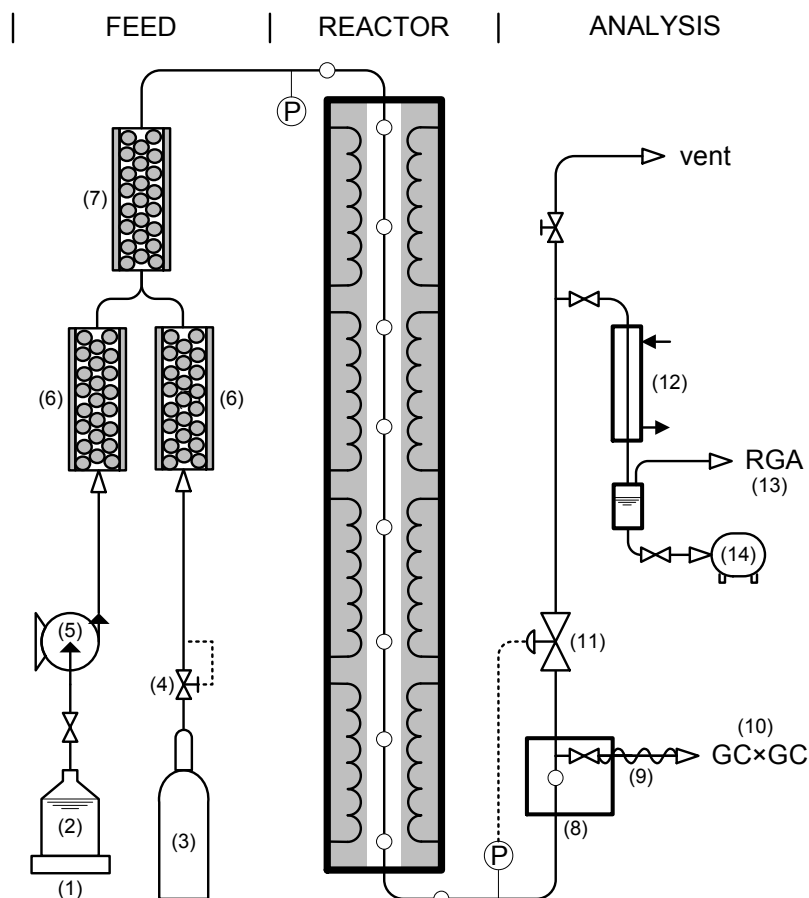# Section S1: Experimental Setup

Reactor Overview

Figure S-1 shows a schematic overview of the reactor setup, which was discussed extensively elsewhere [1-3].

Figure S-1: Bench-scale reactor setup at the Laboratory for Chemical Technology

1: electronic balance, 2: JP-10 container, 3: gaseous diluent (N2), 4: coriolis mass flow controller, 5: peristaltic pump, 6: evaporator, 7: quartz beads filled mixer, 8: heated sampling oven, 9: heated transfer lines, 10: GC×GC, 11: pressure regulator, 12: condenser, 13: refinery gas analyzer, 14: condensate drum.

JP-10 is fed by a peristaltic pump (Heidolph PD 5201, Germany) and the flow rate is determined by an electronic balance monitoring the mass of the JP-10 container. The liquid reactant (mainly exo-TCD: boiling point 457K [4]) flows through a vaporizer kept at 523K filled with quartz pellets to allow a smooth evaporation. Gaseous nitrogen is heated parallel to JP-10 and mixed with it downstream of the vaporizer. The mass flow rate of nitrogen is controlled by a coriolis mass flow controller (Gefran - Bronkhorst Cori-Tech, mini CORI-FLOW®, M1x). To ensure homogeneous gas-gas mixing, a mixing volume filled with quartz pellets is placed upstream of the reactor. The tubes from the evaporator/heater to the mixing unit are heated to prevent condensation. The reactor pressure was controlled by a valve which is placed downstream of the reactor. The pressure drop over the reactor is negligible under normal operating conditions. Eight thermocouples are placed at the various positions along the reactor length to measure the process gas temperature (Fig. S-2).
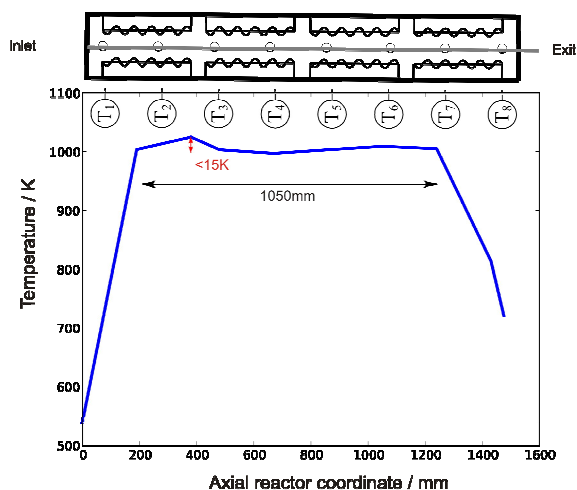

Fig. S-2: Process gas temperature profile along the axial reactor coordinate measured by the eight thermocouples corresponding to a set temperature in the isothermal section of 1003 K.

The furnace is divided into four separate sections, controlled by four thermocouples. The feed mixture enters the reactor and is heated to the set temperature in a section of 0.200 m. A quasi-isothermal zone of 1.050 m is the main pyrolysis zone. The heating of the inlet gas causes a small temperature overshoot of the set temperature of less than 15 K in the first 0.100 m downstream of the heating section. Temperature variations along the remaining part of the isothermal pyrolysis zone remain within ± 5 K. The isothermal pyrolysis zone is followed by a zone of 0.200 m with a steep temperature decrease to 623 K maintained at the sampling box.

Settings and characteristics of the analysis section

Comprehensive two-dimensional gas chromatography has shown to be a powerful tool for the on-line analysis of complex hydrocarbon mixtures [5]. The combination of an apolar (Rtx-1 PONA, dimethyl polysiloxane, 50m × 0.25mm × 0.5 μm, Restek) and a more polar (BPX-50, 50% phenyl polysilphenylene-siloxane, 2m × 0.15mm × 0.15 μm, SGE) gives rise to an enhanced separation resolution for structurally related components. Fig. S-3 gives a schematic overview of the GCxGC-FID/TOF-MS setup.
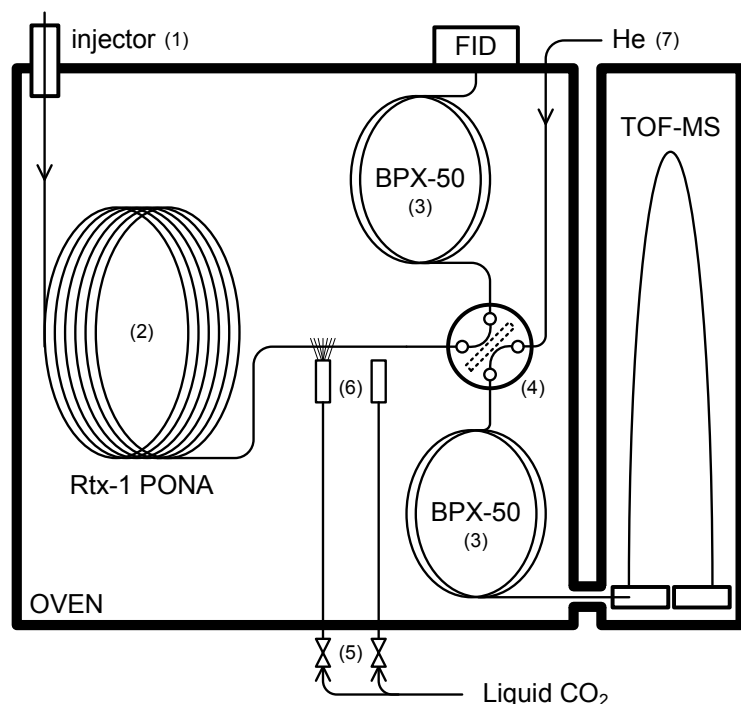
Fig. S-3: A schematic overview of the GCxGC-FID/TOF-MS setup. 1: split/splitless injector, 2: 1st dimension apolar column, 3: 2nd dimension polar column, 4: manual 4-port 2-way valve (FID – TOF-MS switch), 5: solenoid valves, 6: two-jet cryogenic CO_2 modulator, 7: protective helium flow.

Table S-1 gives an overview of the settings and characteristics of the GCxGC-FID/TOF-MS apparatus.

Table S-1: GCxGC-FID/TOF-MS specifications and settings for on-line analysis

Injection	split ratio: 95, split flow 199 ml min^{-1}, 523.15 K
Carrier gas	He, constant flow (2.1 ml min^{-1})
First column	Rtx-1 PONA[a] (50 m x 0.25 mm x 0.5 μm)
Second column	BPX-50[b] (2 m × 0.15 mm × 0.15 μm)
Oven temperature	233.15 K (4 min hold) $\rightarrow$ 4 K min^{-1} $\rightarrow$ 523.15 K (0 min hold)
Detector	FID (range: 10 or 1) and TOF-MS
Modulation period	4 s (using CO_2)
Modulation delay	15 min

[a] **dimethyl polysiloxane (*Restek*);** [b] **50 % phenyl polysilphenylene-siloxane (*SGE*)**

Response factors for many important larger hydrocarbons (cyclopentene, benzene, toluene, ethylbenzene, xylenes, styrene, indene, naphthalene and exo-TCD) were experimentally

determined by injecting known mixtures of these components (Table S-2). Response factors for other minor hydrocarbons were calculated using the effective carbon number concept [6].

Table S-2: Experimentally determined response factors (RF) for important species for peaks quantified using the FID of the GCxGC setup.

Component	RF	Component	RF
Methane	1.000	Xylenes	0.830
Cyclopentene	0.944	Styrene	0.850
Benzene	0.844	Indene	0.925
Toluene	0.849	Naphthalene	0.884
Ethylbenzene	0.907	Exo-TCD	0.860

A TEMPUS ToF-MS (Thermo Scientific, Interscience) is used. Electron impact (EI) ionization was performed at 70 eV, a detector voltage of 1700V was applied and the acquisition frequency was set at 30 spectra s^{-1} in a mass range of 35-400 amu. The data obtained with ToF-MS was acquired using thermo Scientific's Xcalibur software. The raw $GC \times GC$ data files were processed using HyperChrom, i.e. the Chrom-Card extension for $GC \times GC$ data handling that enables 3D representation as well as the common color plot representation of the data. HyperChrom also allows automatic 3D peak quantification and identification. The latter is accomplished by cross referencing the measured mass spectra to the spectra in the available MS libraries.

Parallel to the effluent analysis at high temperature, the reactor effluent is further cooled down to below 423 K by passing it through a water cooled condenser and cyclone to remove liquids and tars. The gaseous fraction of this stream is sent to a dedicated gas chromatograph (GC). Table S-3 shows the settings and characteristics of the GC used to quantify C_{4-} components.

Table S-3: Settings and characteristics of the GC for on-line analysis of C_{4-} components.

Specification	Channel 1 TCD-R	Channel 2 TCD-L		Channel 3 FID
Injection	250 µl (gas) 353.15 K	250 µl (gas) 353.15 K		50 µl (gas) 53.15 K
Carrier gas	N_2	He		He
Pre-column	Hayesep T (1 m×3.2mm)	Hayesep Q (0.25 m×3.2mm)		Rtx-1[a] (15 m×0.53mm×3 µm)
Analytical columns	Carbosphere (2 m×3.2mm)	Hayesep N (1 m×3.2mm)	Molsieve 5A (1 m×3.2mm)	Rt-Alumina BOND[b] (25 m×0.53mm×15 µm)
Oven temperature	353.15 K (isothermal)	353.15 K(isothermal)		$323.15\ K \to 5\ K\ min^{-1} \to 393.15\ K \to 25\ K\ min^{-1} \to 473.15\ K$
Detector	TCD,433.15 K	TCD,433.15 K		FID, 483.15 K

[a] dimethyl polysiloxane (*Restek*); [b] Al_2O_3/KCl (*Restek*)

The secondary TCD channel on the GC (TCD-R) only detects dihydrogen, and uses a dinitrogen as a carrier gas rather than He, to avoid peak interference. Response factors for the quantified components on FID and TCDs of the GC are reported in Table S-4 and Table S-5.

Table S-4: Experimentally determined response factors (RF) for important species for peaks quantified using the FID of the GC setup. Calibration mixture SAPHIR C1-C4 – from Air Liquide.

Component	RF	Component	RF
CH4	1.000	C2H2	0.756
C2H6	0.923	trans-2-C4H8	0.905
C2H4	0.852	1-C4H8	0.824
C3H8	0.920	i-C4H8	0.858
C3H6	0.847	cis-2-C4H8	0.906
i-C4H10	0.900	1,3-C4H6	0.808
n-C4H10	0.884	1-C3H4	0.845
1,2-C3H4	0.832		

Table S-5: Experimentally determined response factors (RF) for important species for peaks quantified using the TCD of the GC setup. Calibration mixture SAPHIR C1-C4 – from Air Liquide.

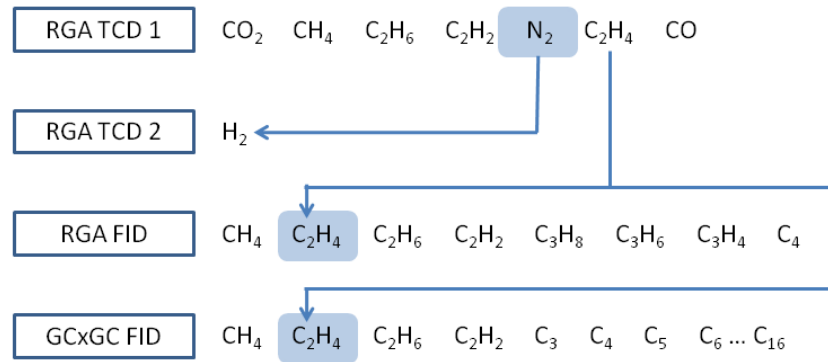| Component	RF	Component	RF
H2	0.097	C2H6	1.538
N2	1.422	C2H2	1.632
C2H4	1.544	CH4	1.000

Calculation of mass flow rates

Mass flow rates of dihydrogen, methane, and molecules containing two carbons are calculated as using the absolute flow rate of dinitrogen gas as the reference (Eq. S-1).

$$\dot{m}_i = \frac{f_i \cdot A_i}{f_{N2} \cdot A_{N2}} \cdot \dot{m}_{N2}$$

<div align="right">**Eq. S-1**</div>

With:

- A_i, A_{N2} peak areas of component 'i' and dinitrogen respectively

- f_i, f_{N2} response factors of component 'i' and dinitrogen respectively

- m_i, m_{N2} mass flow rates of component 'i' and dinitrogen respectively

With A_i referring to the peak areas measured at the GC-TCD detector. For components on the FID of the GC×GC and GC, ethene was used as a secondary internal standard. Fig. S-4 gives a schematic overview of the use of two internal standards for the calculation of mass flow rates of hydrocarbons.

| RGA TCD 1 | CO_2 CH_4 C_2H_6 C_2H_2 N_2 C_2H_4 CO |

| RGA TCD 2 | H_2 |

| RGA FID | CH_4 C_2H_4 C_2H_6 C_2H_2 C_3H_8 C_3H_6 C_3H_4 C_4 |

| GCxGC FID | CH_4 C_2H_4 C_2H_6 C_2H_2 C_3 C_4 C_5 $C_6 ... C_{16}$ |

<div align="center">**Fig. S-4: Use of reference components for quantitative online effluent analysis**</div>

The two TCDs of the GC are assumed to behave very similar, such that the peak area of dihydrogen measured at TCD-R of the GC can be directly compared to the peak area of the dinitrogen internal standard on TCD-L of the GC. The flow rates of the components '$\dot{m}_i$' are calculated using the ethene flow rate $\dot{m}_{C2H4}$ as the normalization factor (Eq. S-2).

$$\dot{m}_i = \frac{f_i \cdot A_i}{f_{C2H4} \cdot A_{C2H4}} \cdot \dot{m}_{C2H4}$$ Eq. S-2

With:

- A_i, A_{C2H4} peak areas of component 'i' and ethene respectively

- f_i, f_{C2H4} response factors of component 'i' and ethene respectively

- m_i, m_{C2H4} mass flow rates of component 'i' and ethene respectively

Section S2: Overview of experimental operating conditions

Table S-6 shows the operating conditions of the 28 experiments that were carried out. Experiments 1 to 16 are experiments at the lowest dilution level (10 mol% exo-TCD) while experiments 17 to 28 are experiments at the higher dilution level (7 mol% exo-TCD).

Table S-6: Operating conditions of the 28 experiments.

Experiment no [*].	Pressure ($\times$ 10^5 Pa)[#]	T[+] (K)	Mass Flow Rate exo-TCD (10^{-3} kg s^{-1})	Mass Flow Rate N$_2$ (10^{-3} kg s^{-1})	Exo-TCD Conversion (%)
1	1.717	936.6	84	168	4
2	1.723	946.7	84	168	6
3	1.732	956.9	84	168	9
4	1.715	966.6	84	168	11
5	1.765	976.7	84	168	15
6	1.735	987.0	84	168	20
7	1.756	996.5	84	168	27
8	1.734	1006.9	84	168	36
9	1.755	1016.3	84	168	44
10	1.733	1026.0	84	168	53
11	1.710	1035.3	84	168	63

12	1.711	1045.7	84	168	72
13	1.730	1055.9	84	168	79
14	1.748	1066.2	84	168	85
15	1.744	1076.1	84	168	90
16	1.710	1086.3	84	168	94
17	1.719	977.9	84	252	24
18	1.724	987.2	84	252	13
19	1.719	997.0	84	252	18
20	1.703	1006.8	84	252	24
21	1.724	1016.9	84	252	32
22	1.723	1026.7	84	252	42
23	1.723	1036.5	84	252	48
24	1.719	1046.5	84	252	57
25	1.734	1056.4	84	252	66
26	1.757	1066.4	84	252	75
27	1.729	1075.8	84	252	82
28	1.737	1086.4	84	252	89

[*]All measured variables are recorded each time an injection on the analysis hardware is performed. Values reported per experiment are averages of the three analysis runs performed per experimental condition.
[#]corresponds to the measured coil outlet pressure. Negligible pressure drops of less than 100 Pa were observed, but not taken into account.
[+]Tabulated temperature corresponds to the average temperature along the quasi-isothermal reactor coil. Coil inlet and and outlet temperatures are not taken into account because they are significantly lower due to the axial temperature gradients at the ends of the coil.
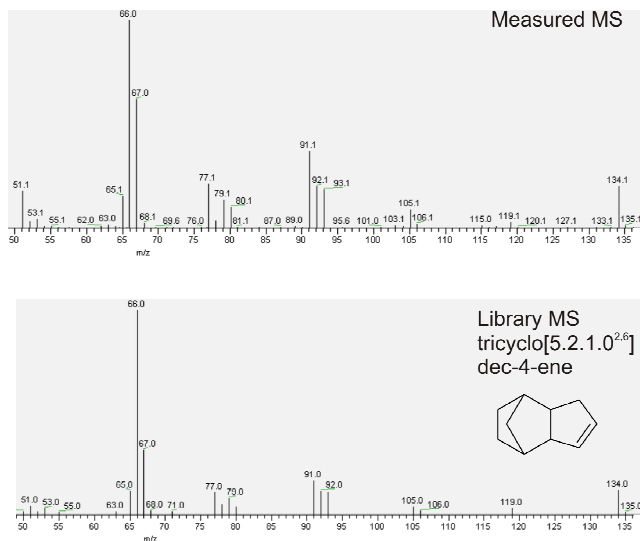
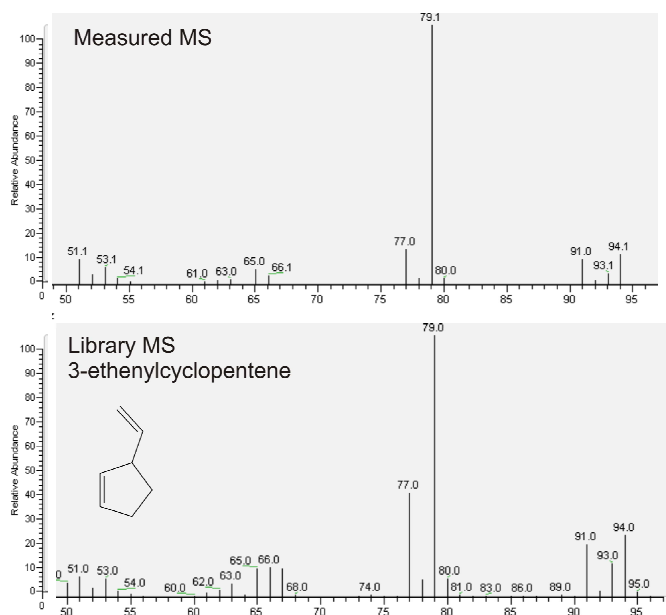# Section S3: Experimental Effluent Data

See file: 'S3 Experimental product data.xls'

Section S4: Mass spectra of selected components

Tricyclo[5.2.1.0^{2,6}]dec-4-ene

Fig. S-5 shows the measured mass spectra and the library entry (NIST Mass Spectral Library v2.6), based on which the measured mass spectra was identified as tricyclo[5.2.1.0^{2,6}]dec-4-ene.

Fig. S-5: Measured and library mass spectra for tricyclo[5.2.1.0^{2,6}]dec-4-ene.

Both spectra showed molecular ions of 134 Da, with major signal peaks at m/z = 66 and 67 corresponding to C_5H_6 and C_5H_7. Lower intensities were observed for m/z = 91, 92 and correspond to the norbornane-type (C_7H_7, C_7H_8) ion fragments.

3-Ethenylcyclopentene

A peak (retention time 31.4 min) to the right of toluene was identified as 3-ethenylcyclopentene (C_7H_{10}). Its mass spectra shows a molecular ion with m/z = 94, an intense signal at m/z = 79 and signals at m/z = 77, 80, 91 and 93 with intensities similar to the library mass spectra, cf.Fig. S-6.

Fig. S-6: Measured and library mass spectra for 3-ethenylcyclopentene.

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