

## Supplementary Materials for

### **Ruthenium-Catalyzed “Open-Loop” Recycling of Polyethylene *via* Tandem Isomerization-Metathesis (ISOMET)**

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#### **This PDF file includes:**

Supplementary Text

Figs. S1 to S12

Tables S1 to S6

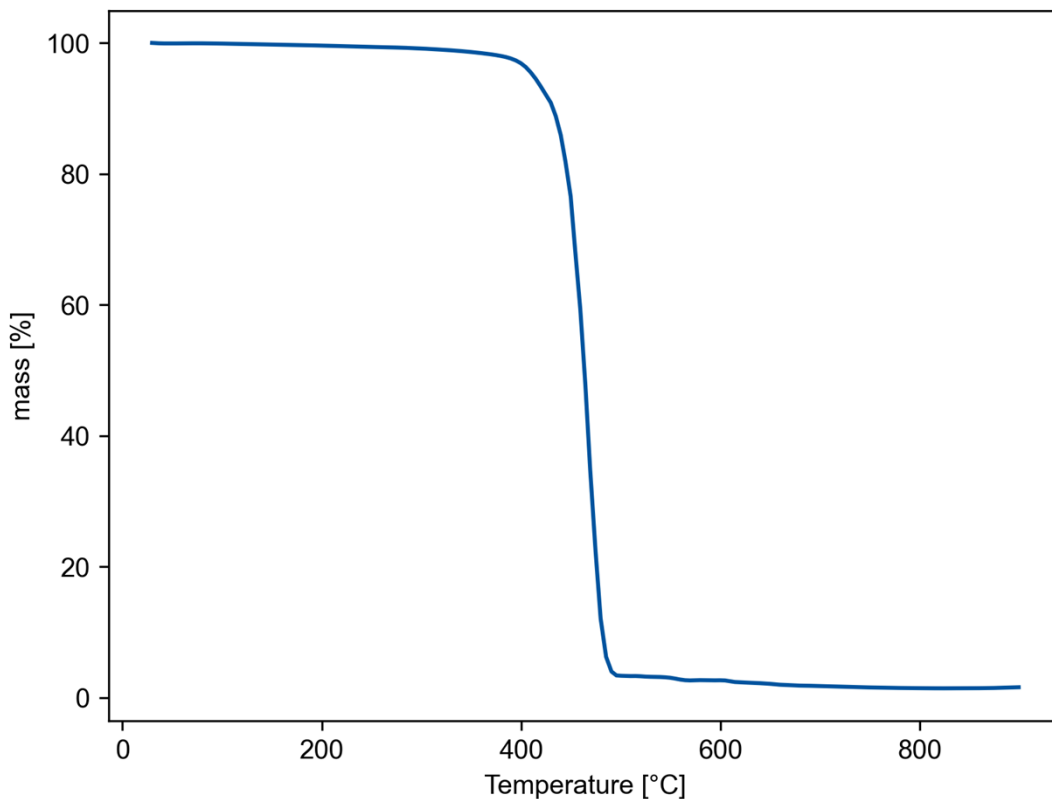
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## 1. Materials and Methods

All metathesis reactions were conducted under nitrogen atmosphere using Schlenk technique or under argon using a glovebox. The reagents and solvents (Aldrich) including deuterated solvents (Eurisotop) were used as received, unless otherwise stated. 1-Octadecene (Aldrich) was filtered through a short pad of activated alumina in the glovebox. Preliminary high-pressure reactions were carried out in a 150 mL Fischer-Porter bottle, using 99.9% purity ethylene (Linde). The gaseous reaction products in the preliminary reactions were analyzed on-line by a Shimadzu GC-2010 gas chromatograph (GC) equipped with a 50-m HP-PLOT-Fused Silica column ( $\text{Al}_2\text{O}_3$ , KCl) and flame ionization detector (FID). The propylene response factor has been calibrated by injecting a predefined amount (in mmol) of gas. GC-MS analyses were carried out using a Shimadzu GCMS-QP2010 Ultra instrument fitted with an ZB-5MSi column for the preliminary reactions. BICAAC metathesis catalysts **1** and **2** were synthesized according to literature procedure.<sup>1</sup> The virgin polymer (Polyethylene TIPELIN, MOL Petrochemicals, CAS: 25213-02-9 (grades made by Phillips technology); 25087-34-7 (grades made by Mitsui technology); melting point: 125 -145 °C; flash point: 350 - 370 °C; Solubility: insoluble in water, soluble in hydrocarbons (80 °C); density: 934 - 964 kg/m<sup>3</sup> (23 °C); Bulk density: 500 - 550 kg/m<sup>3</sup>; MFR flow index (at 190 °C): 2.16 kg load 0.06 - 2 g/10min; 5 kg load 0.26 - 1,3 g/10min; 21.6 kg load 8 - 30 g/10min) was used as received. The municipal HDPE waste was sorted, washed, the labeling was removed, and the clean plastic was shredded. All reactions were conducted under argon atmosphere using Schlenk technique. Semi-batch reactions were carried out in in-house manufactured 20-, 50- and 900-mL autoclaves (figure S12). Toluene was degassed and stored over molecular sieve (4Å) under argon atmosphere. Pyrolysis oils were degassed with argon prior to use. Scaled-up experiments have been carried out using 3.5 grade ethylene (99.95% from Westfalen). The gas analysis of the scaled up experiments have been carried out using on-line Agilent 8860 GC equipped with a Plot Fused Silica column ( $\text{Al}_2\text{O}_3/\text{KCl}$ ) (length: 50 m, inner diameter: 0.32 mm, film thickness: 0.5  $\mu\text{m}$ ), SSL Inlet (temperature: 250 °C, pressure: 0.8 bar, flow: 13.6 mL/min) and FID (temperature: 250 °C, flow: 1.4 mL/min) with helium as carrier gas (oven temperature program: 5 min isothermal at 50 °C, increase to 200 °C with 8 °C/min, then hold 40 min at 200 °C). The propylene response factor has been calibrated by injecting a predefined amount (in mmol) of gas.

## 2. HDPE Pyrolysis reactions



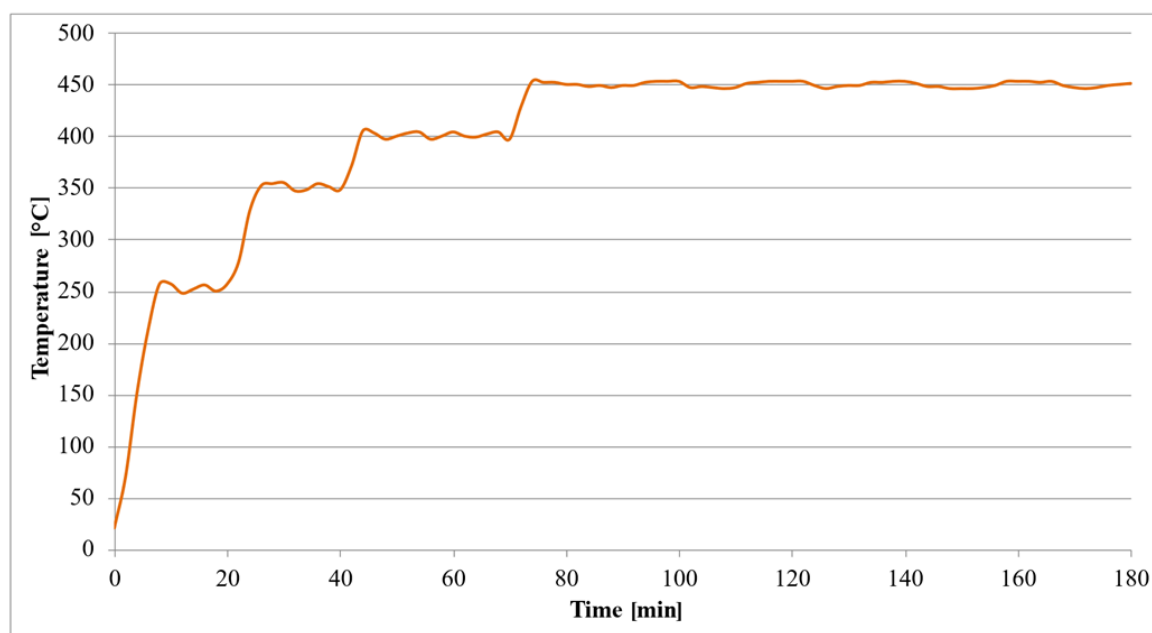
**Fig. S1.:** TGA of TIPELIN 6010B.

### **2.1. Pyrolysis of virgin and post-consumer HDPE plastics**

The pyrolysis test of the virgin HDPE granule was carried out in a batch reactor, where the temperature was gradually raised to 450 °C. The reactor was fitted with a water-cooled heat exchanger to condensate the hydrocarbon vapors into pyrolysis oil. During the first 20 minutes of the test the temperature was raised to 250 °C; between the 20<sup>th</sup> and 40<sup>th</sup> minutes the temperature was set to 350 °C; between the 40<sup>th</sup> and 70<sup>th</sup> minutes of the experiment, the temperature was raised to 400 °C; and after the 70<sup>th</sup> minute the temperature was elevated to 450 °C. The temperature of the reactor as a function of time is shown in figure S1. The measurement was carried out for a total of 3 hours. The

inert atmosphere was ensured by the introduction of nitrogen gas with a flow rate of 2 l/h. The amount of feedstock measured was 750 g of HDPE granulate. During pyrolysis, beside the liquid and gaseous products some solid residue formed. The yields obtained are 89.69% (liquid), 8.65% (gas), 1.66% (solid), respectively. GC-FID analysis of the gas phase showed 26 Vol% propylene and 12 Vol% ethylene. The propylene and ethylene response factor has been calibrated by injecting a predefined amount (in mmol) of gas. Rest of the gas phase involved saturated C1 – C5 hydrocarbons, but these components were not determined quantitatively.

The experiment was also carried out using municipal HDPE plastic waste (typically detergent bottles). During the preparation of the raw material, the bottles were sorted out, cleaned, and shredded. In the experiment with the municipal HDPE waste, the reactor vessel was charged with 340 g of shredded plastic (the mass of shredded plastic per unit volume is lower than that of virgin HDPE granules). The yields of the obtained liquid, gas and solid residues were 62.04%, 12.96% and 25.00%, respectively.



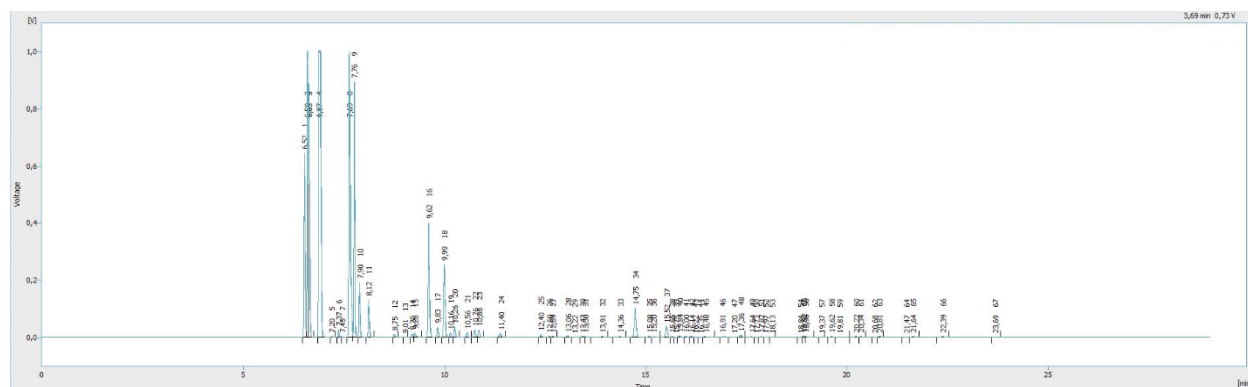
**Fig. S2.:** Temperature profile of HDPE plastic pyrolysis.

## 2.2. Pretreatment of HDPE pyrolysis oils.

Virgin HDPE: The crude pyrolysis oil (16.4 mL, 12.3 g) was fractionated under vacuum (2 mbar) at room temperature for 0.5 hour and then at 100 °C for 1 hour, resulting in a light (5.2 mL, 3.9 g – virgin light, 32%) and a heavy liquid phase (11.2, 8.4 g – virgin heavy, 68%). The light fraction contained volatile compounds up to C10 while the heavy fractions contained mainly  $\geq$  C11 hydrocarbons, predominantly terminal alkenes, alkanes and dienes.

Post-consumer HDPE: The data given below refer to the molecular composition of a crude post-consumer HDPE pyrolysis gas (table S1) and oil (table S2). The crude pyrolysis oils (800 ml) were fractionated under vacuum (2 mbar) at room temperature for 1 hour and then at 100 °C for 2 hours, resulting in a light (300 ml – post-consumer light, 37%) and a heavy liquid phase (500 ml – post-consumer heavy, 63%). The heavy fraction of post-consumer HDPE pyrolysis oil (500 ml) was further purified by filtration through a short plug of alumina to give 400 ml of purified heavy fraction (post-consumer heavy (filtered)). The light fraction contained volatile compounds up to C10 while the heavy fractions contained mainly  $\geq$  C11 hydrocarbons, predominantly terminal alkenes, alkanes and dienes.

According to quantitative GC-MS analysis, the heavy fraction contained 55 wt% alkanes, 40 wt% alkenes and 5 wt% dienes (the response factors of each homologue are shown in table S3).



**Fig. S3.:** GC-FID of pyrolysis gas phase.

**Table S1.:** Peak table of pyrolysis gas phase. (C1-C4 region of the chromatogram, entry13: summary of the full chromatogram).

Peak	Retention time [min]	AUC*	AUC* %	Name
1	6.52	1165	7%	ethane
2	6.59	1987	12%	ethylene
3	6.63	2342	14%	propane
4	6.87	4411	26%	propylene
5	7.20	3	0%	ethyne
6	7.37	43	0%	propadiene
7	7.45	2	0%	butane
8	7.63	2482	14%	trans-but-2-ene
9	7.76	1625	9%	but-1-ene
10	7.90	350	2%	isobutene
11	8.12	246	1%	cis-but-2-ene
12	8.75	20	0%	propyne
13	–	17196	100%	–

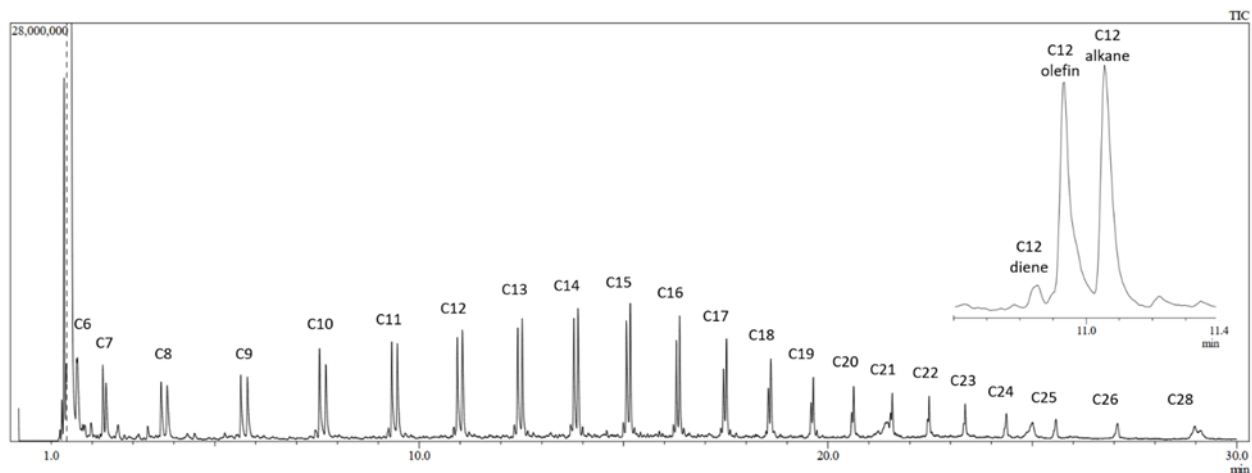
\*AUC: area under the curve

**Table S2.:** Peak table of crude post-consumer HDPE pyrolysis oil (post-consumer crude).

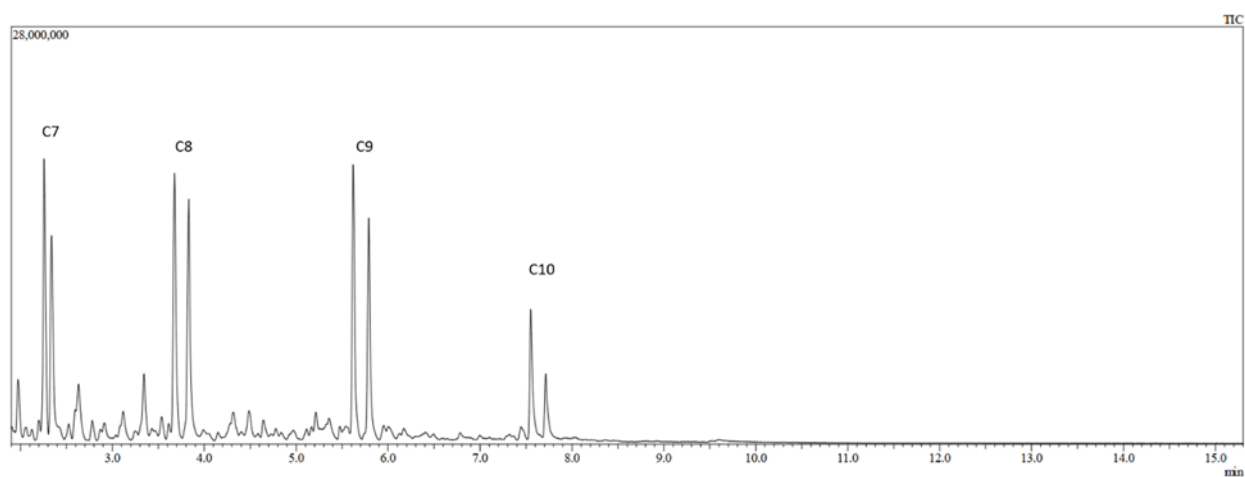
Peak	Retention time [min]	AUC*	Name
1	1.64	18031561	C6 olefin/alkane
2	1.97	2025415	methylcyclopentene
3	2.26	10028191	C7 olefin
4	2.34	8972374	C7 alkane
5	2.63	3125662	methylcyclohexane
6	3.36	2251095	methylcyclohexane
7	3.69	9662438	C8 olefin
8	3.83	10713658	C8 alkane
9	5.63	10121646	C9 olefin
10	5.80	10680491	C9 alkane
11	7.46	940248	C10 diene
12	7.56	16295169	C10 olefin
13	7.72	11781894	C10 alkane
14	9.25	1105932	C11 diene
15	9.33	15808881	C11 olefin
16	9.47	15048878	C11 alkane
17	10.85	1390369	C12 diene
18	10.93	14796526	C12 olefin
19	11.06	16066257	C12 alkane
20	12.33	2192426	C13 diene
21	12.41	15687017	C13 olefin
22	12.52	17478700	C13 alkane
23	13.70	1812213	C14 diene
24	13.78	15997335	C14 olefin
25	13.89	17904801	C14 alkane
26	13.99	1110724	C14 olefin
27	14.99	18031561	C15 diene
28	15.07	1710614	C15 olefin
29	15.16	14045213	C15 alkane
30	15.27	17138606	C15 olefin
31	16.22	699558	C16 diene
32	16.29	1626609	C16 olefin
33	16.37	12110073	C16 alkane
34	16.47	16026267	C16 olefin
35	17.38	1001572	C17 diene
36	17.45	536923	C17 olefin
37	17.52	8860015	C17 alkane
38	17.61	13143041	C17 olefin
39	18.48	749405	C18 diene
40	18.54	442653	C18 olefin
41	18.61	6622474	C18 alkane
42	19.59	9354764	C19 olefin
43	19.64	4454284	C19 alkane
44	19.73	7597008	C19 olefin
45	20.58	876871	C20 olefin
46	20.63	2853284	C20 alkane
47	21.45	5864418	C21 alkanes
48	21.53	5199126	C21 olefin
49	21.57	3423307	C21 alkane
50	22.44	5741472	C22 olefin
51	22.48	2097651	C22 alkane
52	23.36	4253021	C23 olefin/alkane
53	24.37	5596403	C24 olefin/alkane
54	25.00	5101549	C25 alkanes
55	25.58	8984917	C25 olefin/alkane
56	27.08	4451891	C26 olefin/alkane
57	28.98	4190324	C28 olefin/alkane

\*AUC: area under the curve

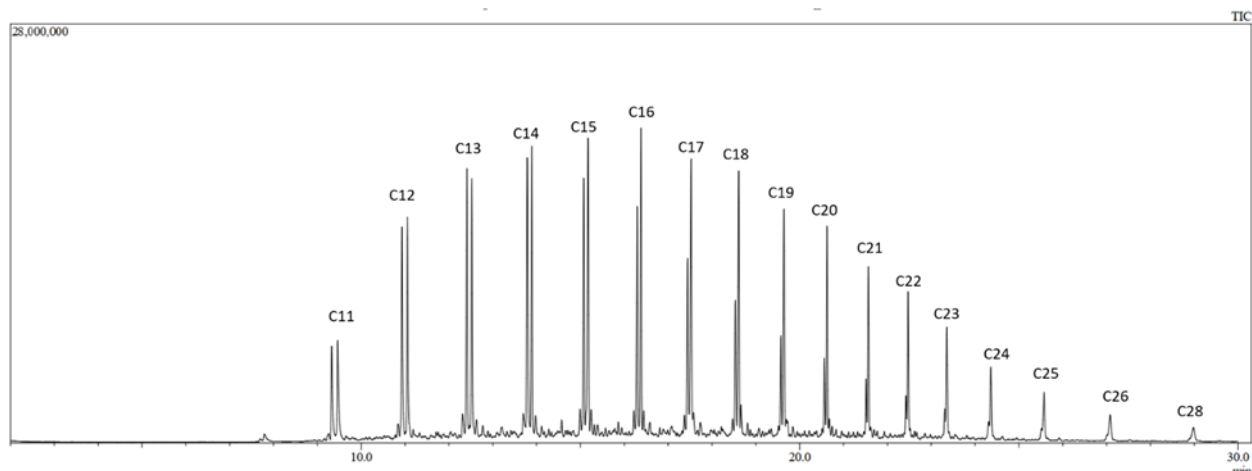




**Fig. S4.:** GC-MS of crude municipal HDPE plastic pyrolysis oil.



**Fig. S5.:** GC-MS of light fraction of municipal HDPE plastic pyrolysis oil.



**Fig. S6.:** GC-MS of heavy fraction of post-consumer HDPE pyrolysis oil.

**Table S3.:** Response factors to 1-octadecene for olefins

Alkane	Response factor
C6	4.50
C7	4.00
C8	3.52
C9	2.99
C10	2.46
C11	2.13
C12	1.79
C13	1.57
C14	1.34
C15	1.24

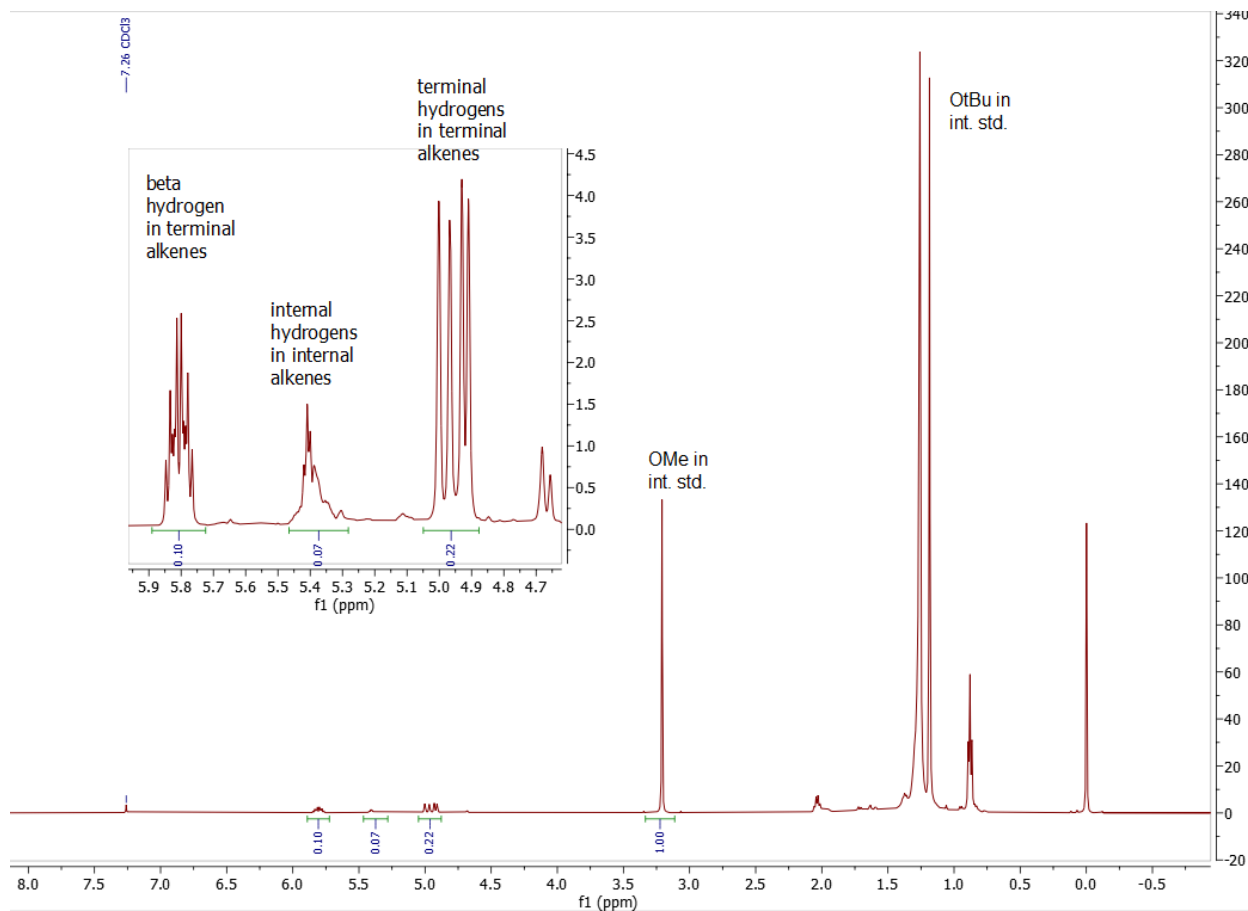
Alkane	Response factor
C16	1.14
C17	1.07
C18	1.00
C19	1.00
C20	1.00
C21	1.00
C22	1.00
C23	1.00
C24	1.00
C25	1.00

Equation for calculation of corrected AUC (area under the curve) for olefins:

$$AUC_{corrected} = \frac{AUC_{C18}^0}{AUC_{C18}} * AUC_{Cn} * RF_{Cn}$$

Where  $AUC_{C18}^0$  denotes the AUC of 1-octadecene in heavy fraction of HDPE pyrolysis oil,  $AUC_{C18}$  denotes the AUC of 1-octadecene in the reaction mixture after ISOMET reaction,  $AUC_{Cn}$  denotes appropriate olefin's AUC in the reaction mixture after ISOMET reaction and  $RF_{Cn}$  denotes the ratio of AUC-s of appropriate olefin and 1-octadecene if equivalent amount is injected on GC-MS.

The double bond content of the heavy fraction is 1 mmol/mL, which was determined by  $^1\text{H}$  NMR measurement with *tert*-butyl methyl ether as the internal standard. The terminal/internal olefin ratio is around 75/25 (fig. S6).

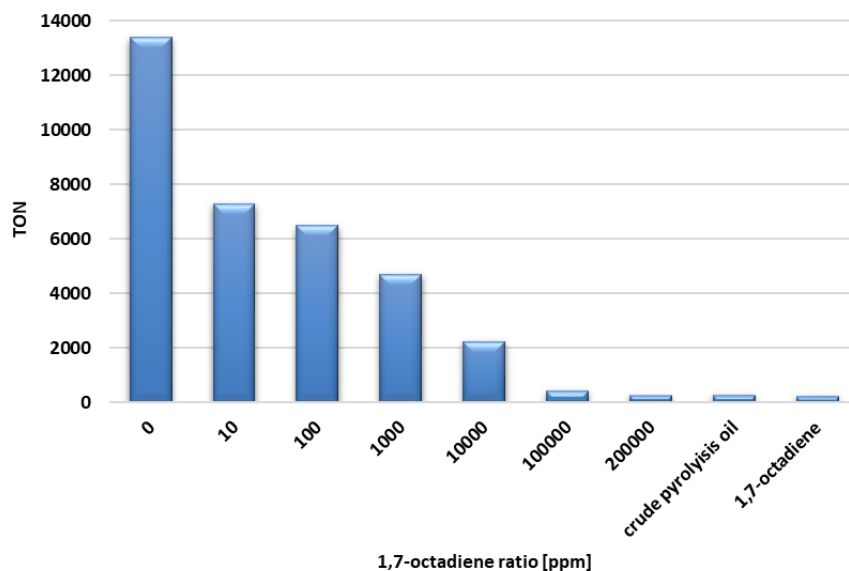


**Fig. S7.:** NMR-quantification of the olefin content in the purified pyrolysis oils.

### 3. Catalytic experiments

#### 3.1. Representative example of the preliminary ISOMET reaction of 1-octadecene in the presence of 1,7-octadiene

In a glovebox, a Fischer-Porter bottle was charged with isomerization catalyst (**RuH**, 3 mg, 3.15  $\mu\text{mol}$ , 0.02 mol%), 1-octadecene (4 g, 15.8 mmol), solution of 1,7-octadecene (1.7 mg, 15.5  $\mu\text{mol}$ , in 170  $\mu\text{L}$  toluene, 0.1 mol%), toluene (3 mL) and the solution of the metathesis catalyst (**2**, 0.096 mg, 0.16  $\mu\text{mol}$ , 0.001 mol% in 100  $\mu\text{L}$  toluene). The Fischer-Porter bottle was closed in the glovebox under argon atmosphere. Then it was brought out of the glovebox and connected to the ethylene line equipped with a pressure gauge. First the ethylene line was purged five times, then the Fischer-Porter bottle was purged five times with ethylene (purity: 3.0; 99.9%). The ethylene pressure was set to 10 bar, the bottle was closed and heated to 75  $^{\circ}\text{C}$  for 3 hours. The reaction mixture was cooled to room temperature and the gas phase was collected for GC-FID analysis. The reaction was carried out with neat 1,7-octadiene and as well as with crude pyrolysis oil.



**Fig. S8.:** Graphical presentation of the variation of turn over number (TON) as a function of the amount of added 1,7-octadiene.

**Table S4.:** Variation of turn over number (TON) as a function of the amount of added 1,7-octadiene.

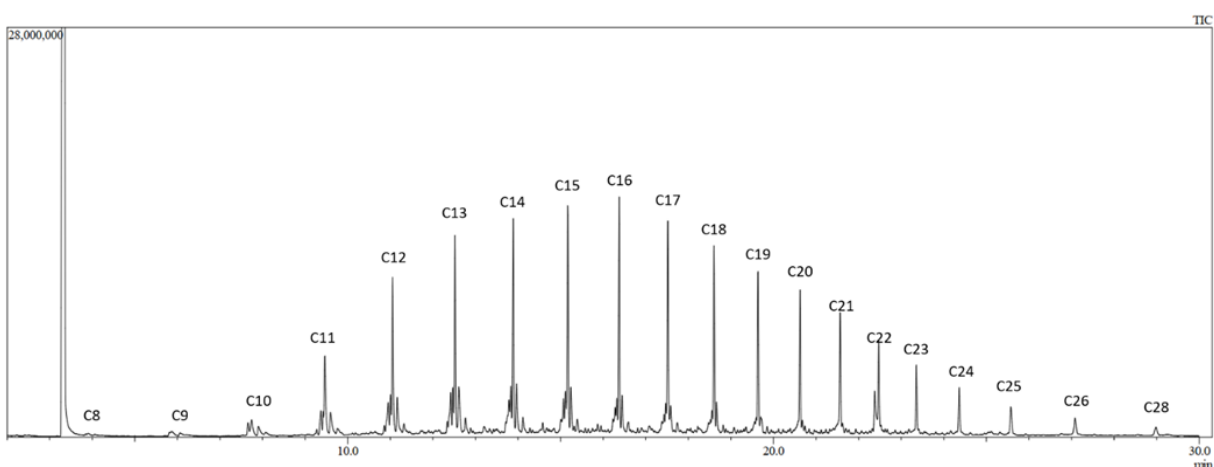
1,7-octadiene [ppm]	TON [mol/mol]
0	13400
10	7300
100	6500
1000	4700
10000	2200
100000	400
200000	200
crude pyrolysis oil	300
1,7-octadiene ( <i>neat</i> )	200

**3.2. Representative example of the ISOMET reaction of 1-octadecene in the presence of different catalyst inhibitors (for table 2)**

In a glovebox, a Fischer-Porter bottle was charged with isomerization catalyst (**RuH**, 3 mg, 3.15  $\mu\text{mol}$ , 0.02 mol%), 1-octadecene (4 g, 15.8 mmol), solution of inhibitor (50 ppm, 0.78  $\mu\text{mol}$  in 150  $\mu\text{L}$  toluene), toluene (3 mL) and the solution of the metathesis catalyst (**2**, 0.096 mg, 0.16  $\mu\text{mol}$ , 0.001 mol% in 100  $\mu\text{L}$  toluene). The Fischer-Porter bottle was closed in the glovebox under argon atmosphere. Then it was brought out of the glovebox and connected to the ethylene line equipped with a pressure gauge. First the ethylene line was purged five times, then the Fischer-Porter bottle was purged five times with ethylene (purity: 3.0; 99.9%). The ethylene pressure was set to 10 bar, the bottle was closed and heated to 75 °C for 3 hours. The reaction mixture was cooled to room temperature and the gas phase was collected for GC-FID analysis.

### 3.3. Representative example of the ISOMET reaction of HDPE pyrolysis oils

In a glovebox, a Fischer-Porter bottle was charged with isomerization catalyst (**RuH**, 20 mg, 21  $\mu\text{mol}$ ), (fractionated) pyrolysis oil (4 mL), toluene (3 mL) and the solution of the metathesis catalyst (**2**, 0.5 mg, 0.8  $\mu\text{mol}$  in 100  $\mu\text{L}$  toluene). The Fischer-Porter bottle was closed in the glovebox under argon atmosphere. Then it was brought out of the glovebox and connected to the ethylene line equipped with a pressure gauge. First the ethylene line was purged five times, then the Fischer-Porter bottle was purged five times with 3.0 ethylene (purity: 3.0; 99.9%). The ethylene pressure was set to 10 bar, the bottle was closed and heated to 75  $^{\circ}\text{C}$ . After 3, 6 and 24 hours, the reaction mixture was cooled to room temperature and the gas phase was collected for GC-FID analysis. At each sampling, the Fischer-Porter bottle was purged three times and refilled with ethylene.



**Fig. S9.:** GC-MS of heavy fraction of post-consumer HDPE pyrolysis oil after ISOMET. The change in the composition of the heavy fraction was determined by integrating the GC-MS chromatogram, which was corrected with the appropriate response factors.

### **3.4. Quantitative conversion of the olefin content of the pyrolysis oil**

**First run:** In a glovebox, a Fischer-Porter bottle was charged with isomerization catalyst (**RuH**, 91 mg, 96  $\mu\text{mol}$ ), (fractionated) pyrolysis oil (1 mL), toluene (4 mL) and the metathesis catalyst (**2**, 7.4 mg, 11.8  $\mu\text{mol}$ ). The Fischer-Porter bottle was closed in the glovebox under argon atmosphere. Then it was brought out of the glovebox and connected to the ethylene line equipped with a pressure gauge. First the ethylene line was purged five times, then the Fischer-Porter bottle was purged five times with 3.0 ethylene (purity: 3.0; 99.9%). The ethylene pressure was set to 10 bar, the bottle was closed and heated to 75 °C. The sampling was carried out at times according to the tables below (table S5). At each sampling, the Fischer-Porter bottle was purged three times and refilled with ethylene. After 24 hours, when no significant amount of propylene formation was observed, the reaction mixture was filtered through a silica plug to remove catalyst impurities.

**Second run:** In a glovebox, the reaction mixture of **Batch 1** was added to a Fischer-Porter bottle alongside with isomerization catalyst (**RuH**, 91 mg, 96  $\mu\text{mol}$ ), toluene (2 mL) and the metathesis catalyst (**2**, 7.4 mg, 11.8  $\mu\text{mol}$ ). Reaction was carried out according to **Batch 1**, with different sampling times.

**Table S5.:** Propylene yield at each sampling point (**Batch 1**).

Time	Propylene			Butene		
	(V%)	[mmol]	[mg] (Yield%)	(V%)	[mmol]	[mg]
<b>First run</b>						
15 min	2.33	1.67	70.3	0.15	0.110	6.1
45 min	3.32	2.37	99.7	0.24	0.174	9.7
75 min	2.82	2.01	84.6	0.25	0.180	10
105 min	1.35	0.97	40.8	0.17	0.124	7.0
165 min	0.79	0.56	23.6	0.17	0.120	6.7
225 min	0.41	0.29	12.2	0.14	0.103	5.8
285 min	0.17	0.12	5.1	0.10	0.073	4.1
405 min	0.11	0.08	3.3	0.14	0.098	5.5
22 h	0.13	0.09	3.9	0.2	0.140	7.9
24 h	0.03	0.02	0.84	0.06	0.044	2.5
Sum 1	11.5	8.18	344.2 (44%)	1.63	1.17	65.4
<b>Second run</b>						
1 h	2.10	1.50	63.0	0.32	0.22	12.3
2 h	1.40	1.00	42.0	0.25	0.18	10.1
3 h	0.76	0.55	22.9	0.16	0.11	6.2
4 h	0.29	0.21	8.6	0.13	0.08	4.5
24 h	1.00	0.72	30.2	0.27	0.19	10.7
Sum 2	5.55	3.97	166.8 (22%)	1.13	0.78	43.8
<b>Cumulative</b>		<b>12.15</b>	<b>511.0 (66%)</b>		<b>1.95</b>	<b>109.2 (21%)</b>

Overall propylene yield is calculated according to the followings:

1 mL HDPE pyrolysis oil is 750 mg ( $d_{\text{pyrolysis oil}} = 0.75 \text{ g/mL}$ ). The mono olefin content is 40%, which is equal to 300 mg. If it is considered that C15 olefin is the statistical mean component, then the **theoretical propylene yield** according to the following equation:

$$\text{C}_{15}\text{H}_{30} (210 \text{ g}) + 12 \text{ C}_2\text{H}_4 (336 \text{ g}) = 13 \text{ C}_3\text{H}_6 (546 \text{ g}) \text{ is } (546/210) * 300 \text{ mg} = \mathbf{780 \text{ mg}}$$

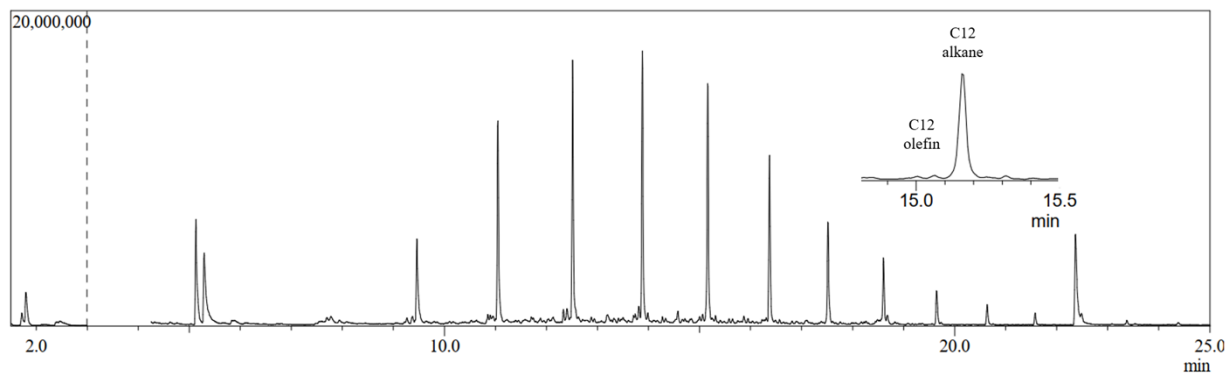
The **propylene yield** is  $(511 \text{ mg}/780 \text{ mg}) * 100 = \mathbf{66\%}$ .

Considering the 109,2 mg butene content it is equal to 163,8 mg of propylene according to the following equation:



$C_4H_8$  (56 g) +  $C_2H_4$  (28 g) = 2  $C_3H_6$  (84 g) (84 g/56 g)\*109.2 mg (butene) = **163.8 mg**

The **cumulative propylene content** can be calculated as 511.0 mg + 163.8 mg = 674.8 mg, **87%**



**Fig. S10.:** GC-MS of heavy fraction of post-consumer HDPE pyrolysis oil after two consecutive ISOMET reactions.

### **3.5. Representative example of the semi-batch ISOMET reaction of 1-octadecene**

20 mL and 50 mL reactions: In a typical reaction, the metathesis catalyst (**1**, table S6) was dissolved in 1-octadecene and toluene under argon in a Schlenk-flask. The isomerization catalyst was weighted into the autoclave under air, which was subsequently closed, evacuated and flushed with argon three times. Then, the 1-octadecene toluene solution was transferred to the autoclave with a syringe through a blank plug-in under a continuous counterflow of argon. After pressurizing the autoclave with ethylene, it was placed into an aluminum cone, which had previously been heated to the desired reaction temperature, on a conventionally stirring plate. The reaction solution was stirred for the desired reaction time. When the reaction was complete, the autoclave was cooled in an ice bath and the gas phase was collected for GC analysis.

**Table S6.:** Applied catalyst and substrate quantities of preliminary ISOMET reactions in 20 mL/50 mL autoclaves.

Autoclave	$V_{substrate}$	$n_{substrate}$	$m_{met.cat.}$	$n_{met.cat.}$	$m_{iso.cat.}$	$n_{iso.cat.}$	$V_{toluene}$
	[mL]	[mmol]	[mg]	[ $\mu$ mol]	[mg]	[ $\mu$ mol]	[mL]
20 mL	5.0	15.6	0.09	0.156	3	3.13	3.0
50 mL	12.5	39.1	0.23	0.391	7	7.81	7.5

900 mL reactions: In a typical reaction, the metathesis catalyst (**2**, 4.15 mg, 7.031  $\mu$ mol, 0.001 mol%) was dissolved in 225 mL 1-octadecene and 135 mL toluene under argon in a Schlenk-flask. The isomerization catalyst (**RuH**, 129 mg, 0.141 mmol, 0.02 mol%) was weighed into the autoclave under air, which was then sealed, evacuated and purged three times with argon. The 1-octadecene toluene solution was transferred to the autoclave using a PTFE cannula through the V-02 valve in an argon atmosphere. The autoclave was then connected to the laboratory plant and pressurized with 10 bar of ethylene through the V-01 bypass. The autoclave was then heated to the target reaction temperature while stirring. After that, it was pressurized with ethylene to the appropriate pressure using a mass flow controller (MFC) and stirred until the desired reaction time. During the reaction, the gas phase of the autoclave was analyzed by GC *in situ* every 90 minutes.

### **3.6. Design-of-Experiment for ISOMET reaction of 1-octadecene in 20 mL and 50 mL autoclaves**

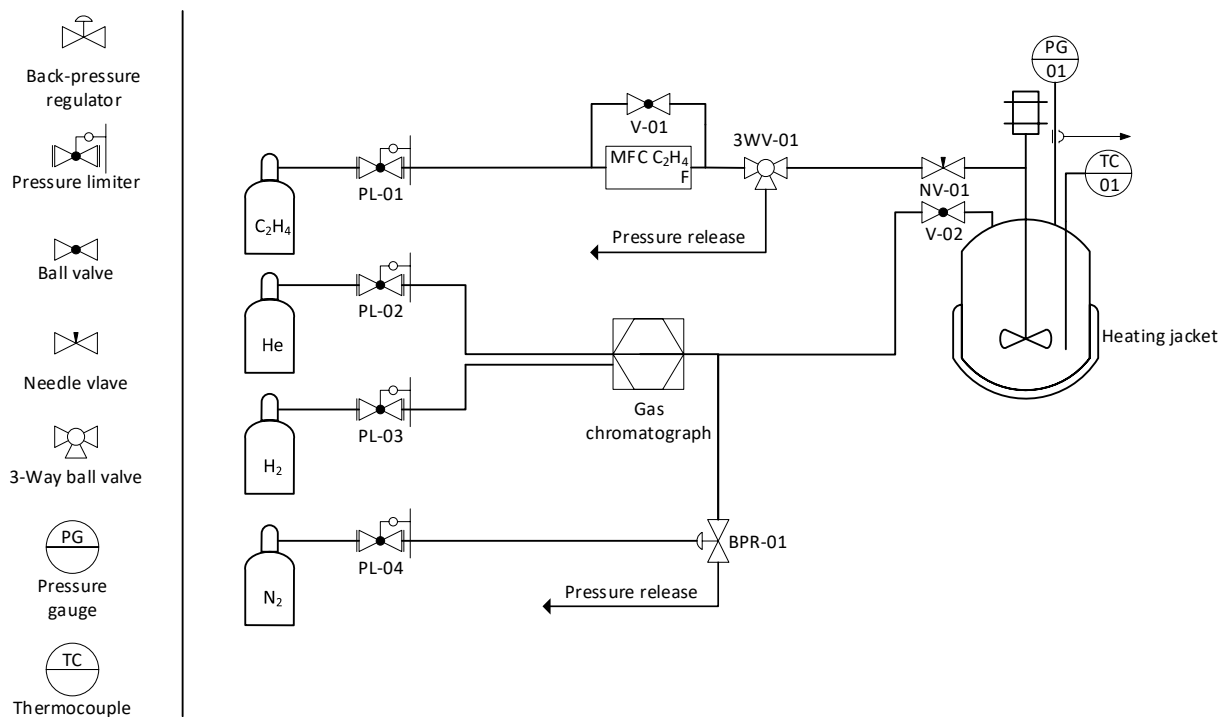
For both Design-of-Experiments (DoE) ethylene pressure and reaction temperature were sampled at 3 different conditions, each. For visualization of the surface plots interpolation and smoothing was applied as implemented in the Python package “scipy”. In detail, the z-data was first interpolated by a cubic function and subsequently smoothed with a filter function.

**Table S7.:** Conditions and results for DoE in 20 mL autoclaves.

Entry	T [°C]	p [bar]	TON [-]
1	80	10	1700
2	80	20	2400
3	80	30	600
4	90	10	3400
5	90	20	9600
6	90	30	750
7	100	10	1400
8	100	20	5200
9	100	30	1350

**Table S8.:** Conditions and results for DoE in 50 mL autoclaves.

Entry	T [°C]	p [bar]	TON [-]
1	90	15	400
2	90	20	2200
3	90	25	570
4	100	15	680
5	100	20	4900
6	100	25	4800
7	110	15	4600
8	110	20	5500
9	110	25	7700



**Fig. S11.:** Laboratory plant scheme for ISOMET reactions in a 900 mL autoclave in batch/semi-continuous mode operation.

### 3.7. Representative example of preliminary ISOMET reactions of HDPE pyrolysis oils in 50 mL autoclaves

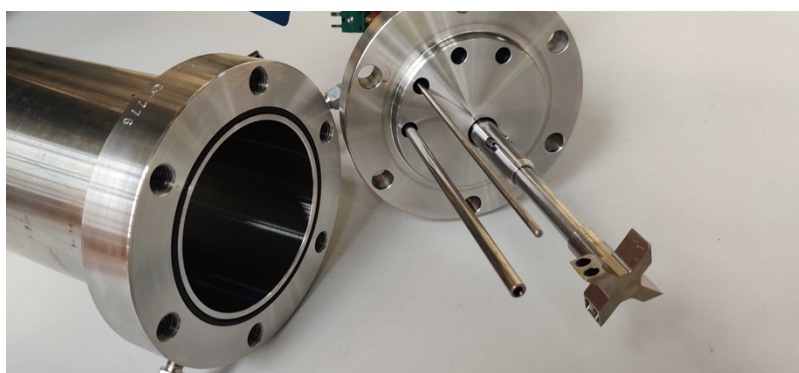
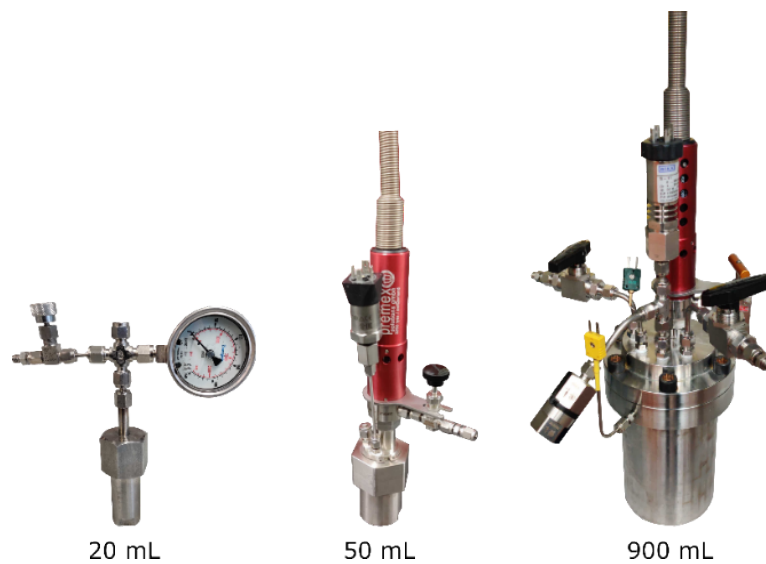
In a typical reaction, the metathesis catalyst (**1**, 1.63 mg, 2.76  $\mu\text{mol}$ , 0.1 mol%) was dissolved in melted HDPE pyrolysis oil heavy fraction (2.5 mL, 2,75 mmol C=C) and toluene (5.5 mL). The isomerization catalyst (20.0 mg, 0.221 mmol, 0.8 mol%) was weighed into the autoclave under air, which was closed, evacuated and flushed with argon three times. Then, the HDPE pyrolysis oil toluene solution was transferred to the autoclave with a syringe through a blank plug-in under a continuous counterflow of argon. After pressurizing the autoclave with ethylene, it was placed into an aluminum cone, which had previously been heated to the desired reaction temperature, on a conventionally stirring plate. The reaction solution was stirred for the desired reaction time. When the reaction was complete, the autoclave was cooled in an ice bath and the gas phase was collected for GC analysis.

### 3.8. Representative example of preliminary ISOMET reactions of municipal HDPE pyrolysis oils in 900 mL autoclave

In a typical reaction, the metathesis catalyst (**2**, 68,0 mg 0,110 mmol, 0,09 mol%) and the isomerization catalyst (**RuH**, 808 mg, 0,880 mmol, 0,7 mol%) were weighted into a Schlenk-flask under argon. Previously melted pyrolysis wax (110 mL, 121 mmol C=C) and 250 mL toluene were added to the reaction mixture under argon. The autoclave was closed and evacuated and flushed with argon three times. The HDPE pyrolysis oil toluene solution was transferred to the autoclave using a PTFE cannula through the V-02 valve in an argon atmosphere. The autoclave was then connected to the laboratory plant and heated to 90 °C and subsequently pressurized to 8 bar of ethylene through the V-01 using a mass flow controller (MFC) while stirring. During the reaction, the gas phase of the autoclave was analyzed by GC *in situ* every 60-90 minutes.



**Fig. S12.:** Picture of laboratory plant used for carrying out ISOMET reactions in 900 mL.



**Fig. S13.:** : Autoclaves used for semi-batch reactions.

#### 4. References

- 1) M. Nagyházi, Á. Lukács, G. Turczel, J. Hancsók, J. Valyon, A. Bényei, S. Kéki and R. Tuba, *Angewandte Chemie International Edition*, 2022, **61**, e2022044.