

Supporting Information

Low Pressure Ethenolysis of a Renewable Methyl Oleate in a Microchemical System

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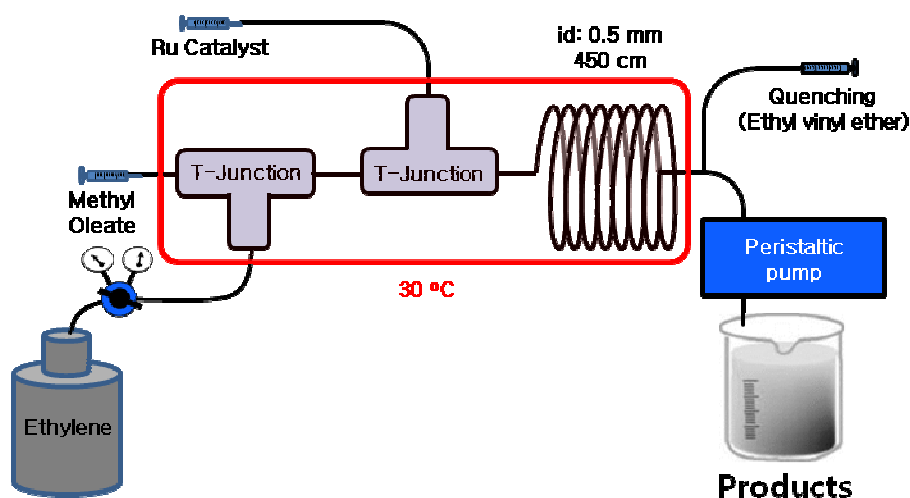
General experimental conditions: Methyl oleate (97%) was purchased from Sigma-Aldrich and purified by alumina treatment prior to use. Ruthenium complexes **6** - **10** were used as provided by Materia, Inc. USA. Ruthenium complex **11** was prepared according to literature procedure.¹ GC spectra were recorded on an Agilent 5975C GC/MSD System (Agilent Tech., USA/Germany), anhydrous toluene purchased from Sigma-Aldrich was used for dissolving the ruthenium catalysts and as an internal standard in the analysis. MiChS-(β) micromixer was obtained from MiChS Co., Ltd. Japan.

General procedure for the ethenolysis of methyl oleate (in optimized microchemical system, design B in figure 1S): The appropriate ruthenium catalyst (1.0 mg) in toluene (2 mL) and methyl oleate (10 mL) were loaded into separate syringes. The ruthenium catalyst solution and methyl oleate were injected at flow rates in the range of 1 - 20 μ L/min and mixed by MiChS-(β) micromixer in the first cooling zone. The pressure of injected ethylene

¹ Anderson, D. R.; Lavallo, V.; O'Leary, D. J.; Bertrand, G.; Grubbs, R. H. *Angew. Chem. Int. Ed.*, **2007**, *46*, 7262-7265

was regulated from 15 to 60 psi. The total retention time in the capillary microreactor was controlled by the length of micro-tube and pumping speed of a peristaltic pump connected to the end of the tube. To terminate the reaction excess ethyl acetate solution of ethyl vinyl ether was added before the tubing reached the peristaltic pump. The results were monitored by GC analysis; peak areas were referenced to the toluene peak.

A) Initial design



B) Optimized design

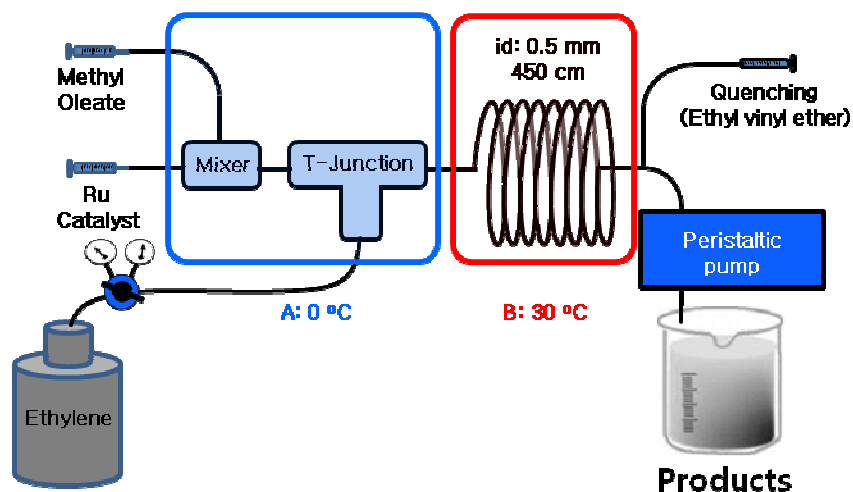


Figure 1S. The microchemical systems for ethenolysis of methyl oleate.

Table 1S. Ethenolysis under Different Temperature and Pressure Conditions
(Figure 2 in the manuscript).

A) 60 psi, 30 °C

Entry	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1	10	10	99	9.9
2	20	18	98	17.6
3	40	36	98	35.3
4	60	46	97	44.6
5	90	60	97	58.2
6	120	65	96	62.4
7	180	65	92	60.5

B) 30 psi, 30 °C

Entry	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1	10	8	97	7.8
2	20	16	94	15.0
3	40	26	91	23.7
4	60	37	90	33.3
5	90	47	86	40.4
6	120	48	85	40.8
7	180	51	81	41.3

C) 30 psi, 40 °C

Entry	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1	10	10	95	9.5
2	20	18	93	16.7
3	40	30	86	25.8
4	60	36	80	28.8
5	90	44	78	34.3
6	120	50	72	36.0
7	180	53	66	35.0

D) 30 psi, 20 °C

Entry	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1	10	4	98	3.9
2	20	11	98	10.8
3	40	21	96	20.2
4	60	27	94	25.4
5	90	33	91	30.0
6	120	36	89	32.0
7	180	42	86	36.1

E) 15 psi, 30 °C

Entry	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1	10	7	85	6.0
2	20	14	85	11.9
3	40	27	80	21.6
4	60	33	76	25.1
5	90	41	70	28.7
6	120	46	65	29.9
7	180	49	61	29.9