

Supporting Information

To the manuscript:

Ruthenium-Catalyzed Hydroformylation: From Laboratory to Continuous Miniplant Scale

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1 Optimization of reaction conditions

1.1 Variation of 1-octene concentration in solvent system DMF/*n*-heptane

Table S1

Entry	1-octene [w%]	Conv. [%]	Y [%]				Leaching [%]	
			C ₉ -aldehydes	C ₉ -alcohols	octane	<i>n</i> -octene	Ru	P
S1.1 ^[a]	20	94	70	9	2	13	-	1
S1.2	13	93	53	2	2	36	2	1.3
S1.3	10	66	14	1	1	50	1.7	0.7
S1.4	7	60	0	0	0	60	1	0.7
S1.5 ^[b]	13	97	66	5	2	24	3.3	4.5
S1.6 ^[b]	7	97	52	5	4	36	3.3	3

Conditions: 1.6 g DMF, 2.4 g *n*-heptane, Ru₃(CO)₁₂ = 0.2 mol%, [L-1]/Ru = 1.1/1, p = 30 bar (CO/H₂ = ½), T = 100°C, t = 5 h, 700 rpm, multiplex autoclaves, T_{sep.} = 0°C. [a] = monophasic reaction mixture after reaction due to alcohol formation; [b] = catalyst concentration regarding solvent volume, not alkene.

1.2 Variation of extraction solvents

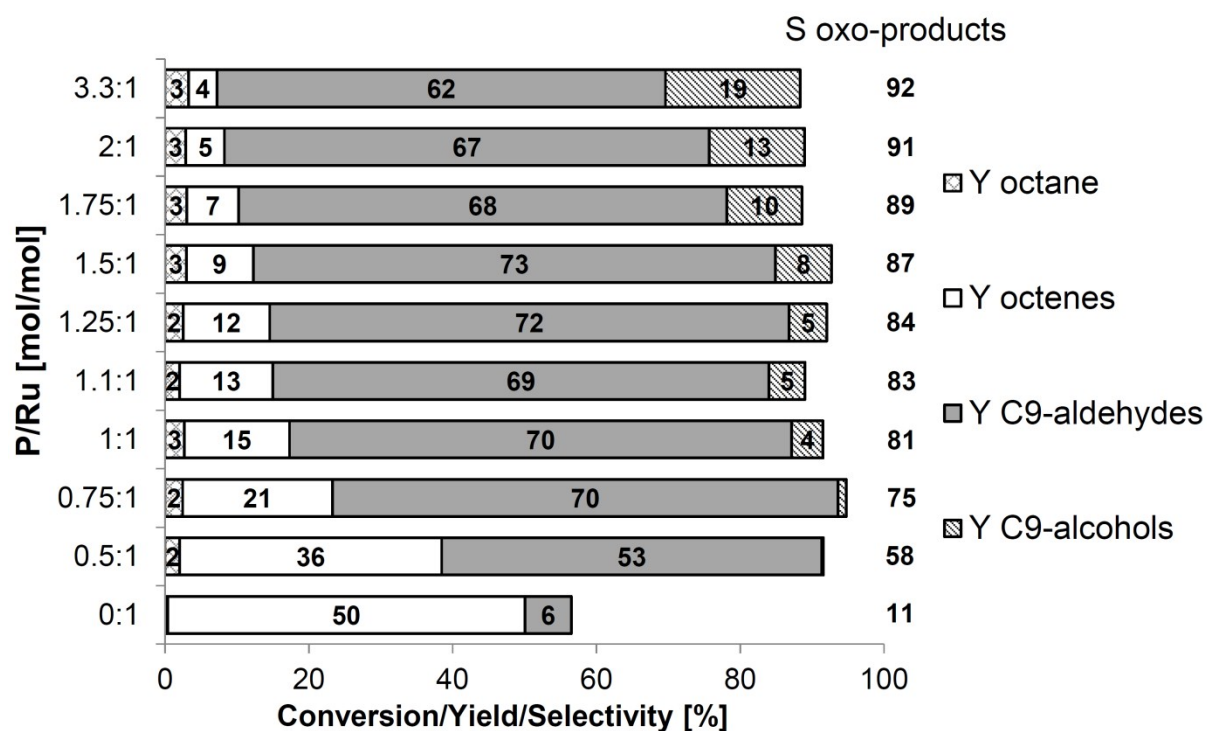
Table S2

Entry	Solvent	Leaching Ru		Leaching P		Product separation [%]	Price ^[a] €/L
		[ppm]	[%]	[ppm]	[%]		
S2.1	<i>n</i> -pentane	36	4.3	14	4.9	60	118
S2.2	<i>n</i> -heptane	26	3.2	12	4.4	58	92
S2.3	<i>iso</i> -octane	22	2.8	8	3.0	57	97
S2.4	<i>n</i> -dodecane	15	1.9	4	1.5	54	552
S2.5	cyclohexane	55	6.4	18	6.2	55	51
S2.6	cyclooctene	48	5.7	17	6.0	-	133

Reaction conditions: Ru₃(CO)₁₂ = 0.2 mol%, [L-1]/Ru = 1.1/1, n(1-octene) = 89.1 mmol = 10 g, 40g DMF, T = 100°C, p = 30 bar (CO/H₂ = ½ at start, then 1/1 semi-batch), t = 2 h, 700 rpm, 300 mL Parr-autoclave.

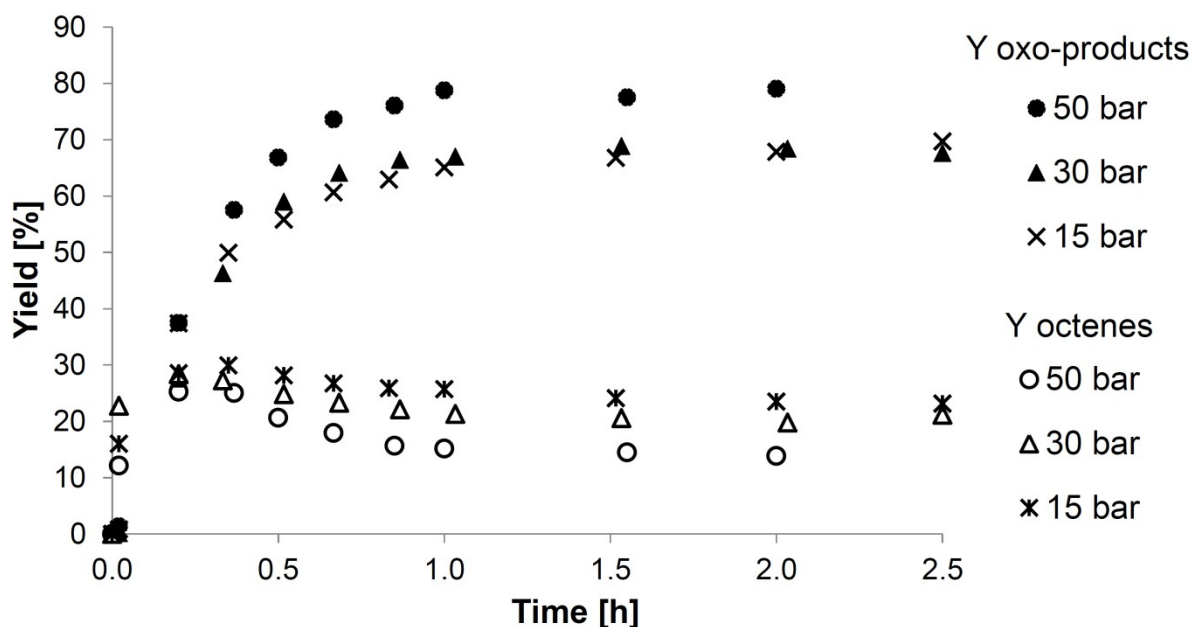
Extraction conditions: DMF/solvent = 1/1.5, t = 0.25 h, 700 rpm, T_{sep} = 0°C, t_{sep} = 1 h, [a] prices from Sigma-Aldrich (01.01.2016)

1.3 Varied amount of ligand



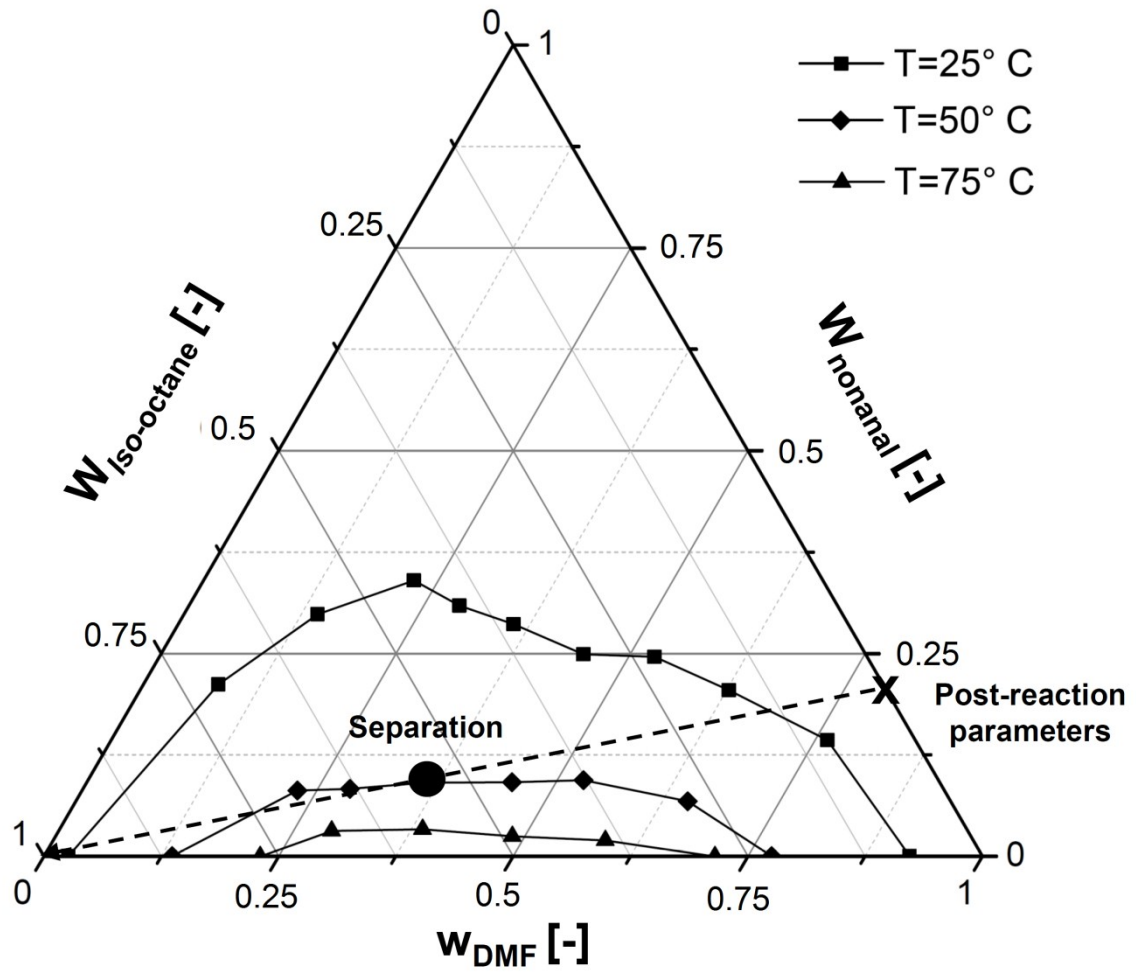
Conditions.: 1 g 1-octene (8.91 mmol), 4 g DMF, $\text{Ru}_3(\text{CO})_{12}$ = 0.2 mol%, L-1, p = 30 bar ($\text{CO}/\text{H}_2 = 1/2$), T = 100°C, t = 5 h, 700 rpm, 6er-Multiplex-autoclaves

1.4 Influence of pressure on the yield of aldehydes and *n*-octenes



Conditions: 10 g 1-octene (89.1 mmol), 40 g DMF, $\text{Ru}_3(\text{CO})_{12}$ = 0.2 mol%, L-1/Ru = 1.1/1, $\text{CO}/\text{H}_2 = 1/2$, semi-batch: $\text{CO}/\text{H}_2 = 1/1$, T = 100 °C, 700 rpm, 300 mL Parr autoclave

1.5 Ternary phase diagram



2 Materials and methods

2.1 Materials

Materials	Purity
$\text{Ru}_3(\text{CO})_{12}$	47% ruthenium
L1*	> 90 %
L2	99%
TPPMS*	>90%
1-octene	99+%
<i>N,N</i> -Dimethylformamide (DMF)	99+%
Propylene carbonate	99.7%
Dimethyl sulfoxide (DMSO)	99.99%
<i>N</i> -Methyl-2-pyrrolidone	99%
<i>n</i> -Heptane	99%
2,2,4-Trimethylpentane (<i>iso</i> -octane)	98%
CO	98%
H ₂	99.999%
N ₂	99,99%

*TPPMS = triphenylphosphine-monosulfonate-sodium salt

2.2 Methods

2.2.1 Batch and semi-batch reaction in laboratory scale

Experiments in laboratory scale were performed in 25 mL “Multiplex”-autoclaves and 300 mL *Parr*-autoclaves. Before preparation the autoclaves were flushed with argon.

The use of 25 mL “Multiplex”-autoclaves starts with weighing the catalyst and ligand. Then polar solvents and 1-octene were added. The autoclaves were shut and connected with the essential equipment such as temperature control and syngas pipes. CO and H₂ were added separately before the temperature control has been started. After the reaction time the autoclaves were emptied, flushed with argon and prepared for further analyses via GC and ICP (see below).

The 300mL *Parr*-autoclave was used for creating time curves and performing kinetic experiments. After weighing catalyst, ligand and polar solvent the autoclave was closed and installed into the reaction equipment. In comparison to the 25mL autoclaves the mixtures were preformed with syngas and temperature before the substrate was added via a special dosing system. Periodically, manual samples were taken for analysis. The procedure at the end of the reaction was the same as described for 25 mL autoclaves.

2.2.2 Miniplant

The initial mixtures containing catalyst, ligand and DMF were prepared for each miniplant apparatus (reactor, mixer, settler, ...). Therefore the substances were weighed into several bottles and flushed with argon. The miniplant-apparatuses were tempered, evacuated and filled with the appropriate mixtures. Then CO was added stepwise in each apparatuses and pipe sections. Then H₂ was added in the similar way. At the beginning of the operation time the pumps for 1-octene, DMF make-up and *iso*-octane were started. Simultaneously, the CO/H₂ to ratio and pressure control were started. During miniplant operation samples were analyzed periodically with an online gas chromatography.

2.3 Analytics

For quantitative analysis of manual samples 0.2 g of the reaction mixture was weighed in a GC vial. Then 0.1 g *n*-decane (external standard) and 0.8 g isopropyl alcohol were added. The contained mass fractions of the substances were determined via gas chromatography (GC) with an HP-INNOWAX column on a HP6890 device. Additionally, each substance was calibrated with the external standard *n*-decane.

Samples of the miniplant operation were determined manually (see above) and via online gas chromatography. The online samples were measured with HP-INNOWAX column on a HP7890 device. The substances were calibrated with an internal standard.

The metal content (ppm) of the product phases was determined with *Thermo Fisher Scientific's* inductively coupled plasma optical emission spectrometry (ICP-OES). The catalyst leaching rate for ruthenium and phosphorus can be calculated with the total amount of the related product fraction, the appropriate mass fraction (ppm) contained, and the initial mass of ruthenium and phosphorus at miniplant start. E.g. 1%/h leaching represents the loss of 1% of initial catalyst amount via product flow in one hour