Electronic Supplementary Information

Understanding the effects of forced and bubble-induced convection in transport-limited organic electrosynthesis

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Materials and methods

The aqueous electrolyte solutions consisted of 0.5 M sodium phosphate (Spectrum Chemical Mfg Corp), 0.03 M EDTA (Fisher Chemical), and 0.02 M tetrabutylammonium hydroxide (Sigma-Aldrich). Before each experiment, 0.1 – 1.0 M AN (TCI Chemicals) was added to 30 ml of the aqueous electrolyte and mixed using a vortex mixer before being inserted into the reactor. Cadmium foil (American Elements) with a 2 cm^2 exposed area was used as the working electrode, and stainless steel foil (McMaster Carr) was used as the counter electrode. The cadmium electrode was stored in an aqueous electrolyte whenever not in use. Electrodes not stored in this way could affect the reactor performance, possibly due to the formation of undesired surface oxides.

Experiments were conducted under constant charge conditions with experiment durations from 4 – 60 minutes and current densities from 20 – 300 mA cm^{-2}. The cell potential is directly related to the current density, shown as linear sweep voltammetry measurements in Fig. S1 for forced and bubble-induced convection at various liquid and gas flow rates.

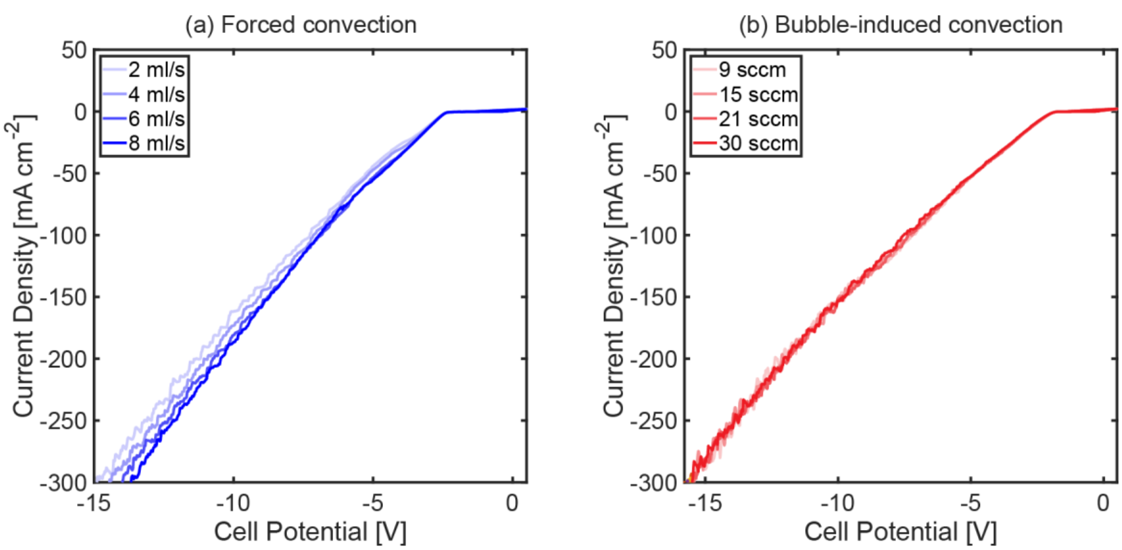

Fig. S1 Linear sweep voltammetry measurements for (a) forced convection and (b) bubble-induced convection across the range of flow rates used in the experiments.

Continuous flow reactors were fabricated with VeroClear Polyjet resin on a Stratasys Objet30 Pro 3D printer. The electrode separation was 1.5 cm, and the cross-sectional area was 1.5 cm^2. An exploded view of the reactor is shown in Fig. S2 and an image of the flow reactor system is shown in Fig. S3. Liquids were circulated using a peristaltic pump (New Era Pump Systems, NE-9000B), and gas (argon) was introduced through a stainless steel frit (40 μm pore size, McMaster Carr) using a computer-controlled mass flow controller (Brooks Instrument, GF40).

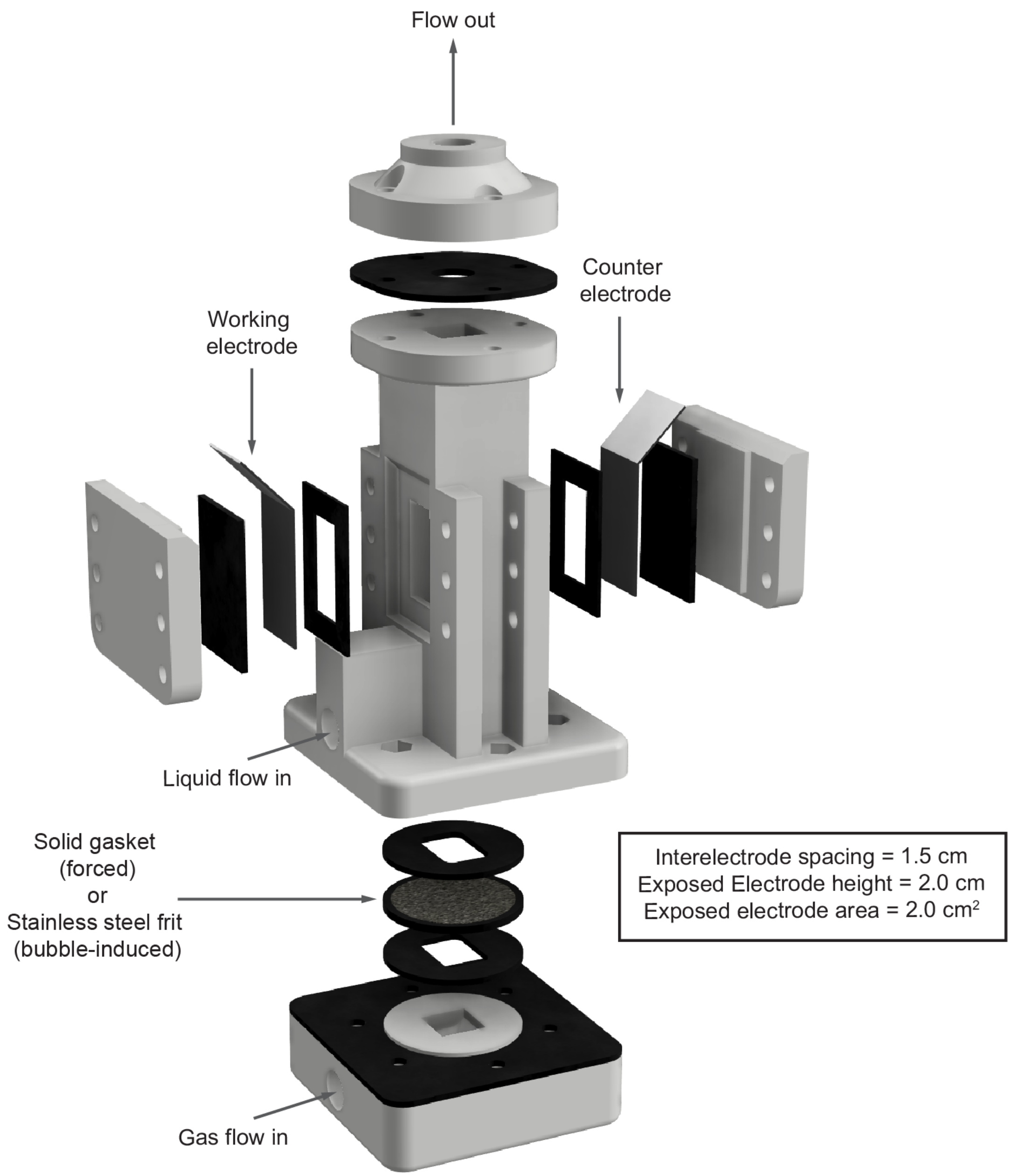

Fig. S2 Exploded view of flow reactor.

Fig. S3 Image of the flow reactor system.

Chemical analysis

After each experiment, the reactor was drained, and 5 ml of the solution was added to a separatory funnel with 10 ml of toluene for liquid-liquid extraction of the organic molecules from the aqueous electrolyte. The organic phase was analyzed with gas chromatography-mass spectrometry (GC-MS, Shimadzu QP2010). Fig. S4 shows the calibration curves for AN, PN, and ADN in electrolytes used to quantify the reaction products.

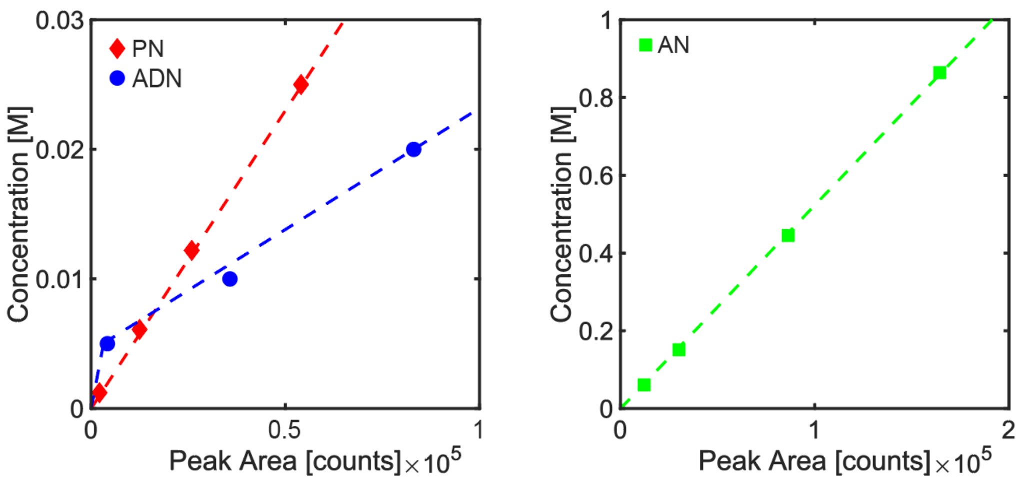

Fig. S4 GC calibration curves for propionitrile (PN), adiponitrile (ADN), and acrylonitrile (AN) relating GC peak area to concentration. Each point represents an average of 3 samples. The detection limit for ADN is ~0.004 M, so the calibration curve has a line to 0 M below 0.005 M to avoid overestimating ADN at low concentrations.

Faradaic efficiency and production rate calculations

Faradaic efficiency for each species produced is calculated by,

$$FE_A = \frac{n_A}{n_{theoretical}} \qquad (S1)$$

where n_A is the moles of species A produced/consumed, determined using GC-MS, and $n_{theoretical}$ is the theoretical total moles produced as determined by Faraday's law,

$$n_{theoretical} = \frac{it}{nF}\ , \qquad (S2)$$

where i is the applied current (A), t is the experimental duration (s), n is the number of electrons involved in the reaction (2 for ADN and PN), and F is Faraday's constant (96,485 C/mol).

The ADN production rate, R_{ADN} (kg cm^{-2} h^{-1}) was calculated using,

$$R_{ADN} = \frac{j_{ADN}}{nF}\left(\frac{3600\ M_{ADN}}{A_{electrode}}\right) \qquad (S3)$$

where j_{ADN} is the partial current density towards ADN (A), M_{ADN} is the molar mass of ADN (kg/mol) and $A_{electrode}$ is the electrode area (cm^2).

Energy calculations

Fig. S5 shows the power required to achieve a particular Sherwood number for forced and bubble-induced convection. For forced convection, the pumping power was calculated using,

$$P = Q\rho g h \,, \tag{S4}$$

where Q is the volumetric flow rate, ρ is the fluid density, g is the acceleration due to gravity, and h is the reactor height. The volumetric flow rate for our reactor ranged from 0.1 – 8 $cm^3\,s^{-1}$, and the reactor height was ~10 cm. Frictional losses due to the walls and viscous losses were negligible (<0.3%).

For bubble-induced convection, the power required was calculated as the power required to compress the gas to a pressure that could overcome the fluid column pressure above the gas inlet. First, the energy required to compress gas from $p_1 = 101.325\ kPa$ to $p_2 = p_1 + \rho g h$ is calculated using,

$$E = -nRT\ \ln\left(\frac{V_2}{V_1}\right), \tag{S5}$$

where n is the moles of gas, R is the ideal gas constant, T is the temperature, and V_i are the initial (i =1) and final (i =2) volumes. To calculate the final volume, we assume an adiabatic process such that,

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \tag{S6}$$

where γ is the isentropic expansion factor (γ = 1.4 for air, γ = 1.66 for ideal monoatomic gas). The energy is then scaled by volume to obtain the energy per unit volume of gas (energy per cm^3) and multiplied by the volumetric flow rate of gas to obtain the power required to supply a particular gas flow rate,

$$P = flow\,rate\ \cdot energy\ per\ cm^3 \tag{S7}$$

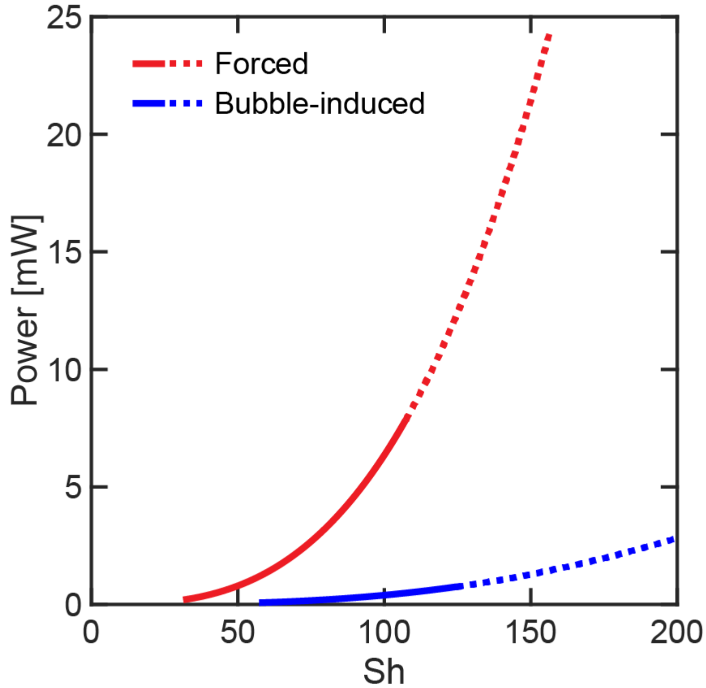

Fig. S5 Power required to achieve a particular Sherwood number for forced and bubble-induced convection. Solid lines indicate the range of Sherwood numbers attainable for each convection method with the flow rates used in this study, and dashed lines indicate higher Sherwood numbers than those used in this study.

Experimental Data

Table 1 Forced convection experimental conditions and results.

Experiment	Time		Current	[AN]	Flow Rate	Sh	FE$_{ADN}$	FE$_{PN}$
	m	s	mA	M	cm^3s^{-1}		%	%
Exp 1	5	0	480	0.78	6.1	98	80.9	8.1
Exp 2	8	34	280	0.91	7.7	106	69.3	2.7
Exp 3	12	0	200	0.31	3.6	82	21.4	68.8
Exp 4	4	26	540	0.10	4.3	87	0.0	30.8
Exp 5	40	0	60	0.94	7.9	107	81.5	1.7
Exp 6	9	14	260	0.49	3.3	80	36.2	59.3
Exp 7	15	0	160	0.37	5.4	94	30.9	63.6
Exp 8	15	0	160	0.83	4.7	90	80.2	4.2
Exp 9	4	37	520	0.86	7.3	104	84.0	2.7
Exp 10	40	0	60	0.57	5.2	93	82.9	6.1
Exp 11	5	0	480	0.72	7.1	103	86.8	9.0
Exp 12	4	0	600	0.43	1.2	57	0.0	73.8
Exp 13	7	4	340	0.99	7.4	105	63.1	4.3
Exp 14	5	13	460	0.23	3.8	84	2.9	58.1
Exp 15	4	17	560	0.71	1.3	59	44.0	45.6
Exp 16	17	8	140	0.14	2	68	0.1	53.8
Exp 17	8	34	280	0.34	0.4	40	0.0	69.8
Exp 18	8	0	300	0.42	1.5	61	5.5	74.7
Exp 19	24	0	100	0.59	2.2	70	72.3	17.4
Exp 20	13	20	180	0.16	4.6	89	0.0	61.1
Exp 21	6	0	400	0.88	0.6	45	69.5	16.4
Exp 22	4	48	500	0.98	3.9	84	70.4	2.2
Exp 23	6	40	360	0.63	4.9	91	73.1	19.3
Exp 24	7	30	320	0.32	6.6	101	9.9	72.9
Exp 25	10	0	240	0.40	6	97	35.2	59.4
Exp 26	6	40	360	0.65	1.1	55	45.6	40.1
Exp 27	30	0	80	0.50	0.1	25	46.2	42.1
Exp 28	24	0	100	0.47	2.7	75	66.4	30.0
Exp 29	5	27	440	0.55	6.4	100	66.6	27.1
Exp 30	10	55	220	0.76	7.6	105	81.5	4.9
Exp 31	6	19	380	0.28	4.1	86	5.5	61.4
Exp 32	60	0	40	0.38	3.1	78	68.0	26.0
Exp 33	4	17	560	0.82	4.4	88	73.9	12.9
Exp 34	17	8	140	0.95	5.5	95	70.3	3.4
Exp 35	8	34	280	0.78	6.9	102	77.1	3.7
Exp 36	7	30	320	0.68	0.3	36	61.3	25.0
Exp 37	5	27	440	0.85	2.9	76	72.1	11.4
Exp 38	4	48	500	0.45	5.7	96	23.7	68.2
Exp 39	6	19	380	0.67	3.4	81	70.2	12.5
Exp 40	5	43	420	0.73	2.7	75	69.5	14.0
Exp 41	4	8	580	0.14	0.9	52	0.0	40.3
Exp 42	12	0	200	0.29	5	92	26.2	60.2
Exp 43	10	55	220	0.23	2.4	72	0.0	62.0
Exp 44	4	26	540	0.26	2.4	72	0.2	57.0
Exp 45	60	0	40	0.90	0.7	48	77.1	4.2
Exp 46	6	0	400	0.61	1.7	64	53.6	26.5
Exp 47	20	0	120	0.52	6.8	102	91.7	5.7
Exp 48	10	0	240	0.53	1.9	66	57.3	14.0
Exp 49	4	0	600	0.19	5.9	97	0.0	45.8
Exp 50	5	13	460	0.21	6.5	100	0.0	52.8

Table 2 Forced convection boundary conditions and results.

Boundary Condition	Time		Current	[AN]	Flow Rate	Sh	FE$_{ADN}$	FE$_{PN}$
	m	s	mA	M	$cm^3 s^{-1}$		%	%
BC1	4	0	600	1.00	0.2	31	46.3	44.0
BC2	4	0	600	1.00	4	85	68.1	1.8
BC3	4	0	600	1.00	8	107	63.0	4.0
BC4	4	0	600	0.50	0.2	31	31.0	54.8
BC5	4	0	600	0.50	4	85	26.7	50.6
BC6	4	0	600	0.50	8	107	39.4	51.1
BC7	8	0	300	1.00	0.2	31	50.8	26.7
BC8	8	0	300	1.00	4	85	66.1	3.9
BC9	8	0	300	1.00	8	107	59.9	3.6
BC10	60	0	40	1.00	0.2	31	74.5	4.5
BC11	60	0	40	1.00	4	85	76.3	1.8
BC12	60	0	40	1.00	8	107	81.9	2.4
BC13	60	0	40	0.50	0.2	31	67.4	22.5
BC14	60	0	40	0.50	4	85	86.6	6.8
BC15	60	0	40	0.50	8	107	88.7	6.5

Table 3 Bubble-induced convection experimental conditions and results.

Experiment	Time		Current	[AN]	Flow Rate	Sh	$\mathbf{FE}_{ADN}$	$\mathbf{FE}_{PN}$
	m	s	mA	M	$sccm$		%	%
Exp 1	6	40	360	0.28	22.8	113	0.0	71.7
Exp 2	6	19	380	0.32	4.2	64	0.0	69.0
Exp 3	13	20	180	0.16	26.6	120	0.0	65.2
Exp 4	4	48	500	0.35	6.7	75	9.3	65.6
Exp 5	5	43	420	0.52	27.9	122	47.4	43.4
Exp 6	15	0	160	0.21	23.2	114	0.0	73.3
Exp 7	30	0	80	0.86	10	86	76.0	2.6
Exp 8	4	0	600	0.59	25.5	118	57.7	26.3
Exp 9	9	14	260	0.77	5.3	69	69.5	11.2
Exp 10	60	0	40	0.57	16	101	88.1	4.8
Exp 11	40	0	60	0.74	12.2	92	80.7	3.9
Exp 12	12	0	200	0.31	7.4	77	0.0	80.2
Exp 13	9	14	260	0.61	19.9	108	80.7	12.9
Exp 14	13	20	180	0.57	3.4	60	69.8	18.7
Exp 15	10	55	220	0.94	17.6	104	74.1	2.9
Exp 16	5	27	440	0.14	10.6	87	0.0	47.5
Exp 17	4	27	540	0.12	18.7	106	0.0	21.5
Exp 18	8	0	300	0.80	8	80	77.3	9.4
Exp 19	5	27	440	0.76	24.4	116	85.9	4.9
Exp 20	4	0	600	0.48	10.2	86	32.8	60.6
Exp 21	4	17	560	0.98	12.3	92	69.9	12.9
Exp 22	7	4	340	0.45	6.1	73	31.9	60.3
Exp 23	4	48	500	0.81	18.2	105	84.3	8.7
Exp 24	5	0	480	0.69	3.9	63	56.0	27.7
Exp 25	4	27	540	0.35	27	120	0.0	74.1
Exp 26	60	0	40	0.20	17.2	103	22.6	56.4
Exp 27	8	34	280	0.44	27.6	121	44.9	50.7
Exp 28	4	48	500	0.39	21.5	111	30.2	52.7
Exp 29	7	30	320	0.84	23.7	115	83.5	4.3
Exp 30	20	0	120	0.73	17	103	83.3	4.1
Exp 31	4	17	560	0.15	22.2	112	10.3	45.3
Exp 32	10	55	220	0.54	9.1	83	63.6	24.0
Exp 33	15	0	160	0.99	8.9	82	70.3	3.9
Exp 34	6	0	400	0.90	13.5	95	76.5	7.3
Exp 35	5	43	420	0.66	20.8	110	76.1	10.4
Exp 36	8	0	300	0.26	14.9	98	1.9	65.2
Exp 37	5	13	460	0.47	14.2	97	37.5	56.9
Exp 38	17	9	140	0.23	13	94	23.9	50.8
Exp 39	24	0	100	0.42	19.3	107	66.2	29.7
Exp 40	10	0	240	0.71	11.5	90	80.5	6.7
Exp 41	6	19	380	0.30	16.1	101	0.0	72.5
Exp 42	4	37	520	0.51	30	125	42.1	55.1
Exp 43	5	13	460	0.96	21.1	110	71.1	9.1
Exp 44	30	0	80	0.39	7.1	76	52.8	40.8
Exp 45	20	0	120	0.83	28.9	123	77.5	3.1
Exp 46	4	8	580	0.89	29	123	79.2	9.3
Exp 47	7	30	320	0.92	4.9	67	67.5	11.8
Exp 48	10	55	220	0.66	24.9	117	78.6	8.0
Exp 49	24	0	100	0.17	25.7	118	0.0	62.1
Exp 50	7	4	340	0.63	14.9	98	66.8	15.0

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BC2	4	0	600	1.00	15	98	63.9	9.8
BC3	4	0	600	1.00	30	125	71.6	6.1
BC4	4	0	600	0.50	3	57	31.1	49.5
BC5	4	0	600	0.50	15	98	34.3	56.7
BC6	4	0	600	0.50	30	125	41.6	46.4
BC7	8	0	300	1.00	3	57	63.2	7.1
BC8	8	0	300	1.00	15	98	70.7	5.2
BC9	8	0	300	1.00	30	125	73.6	4.9
BC10	60	0	40	1.00	3	57	75.9	1.8
BC11	60	0	40	1.00	15	98	79.3	2.2
BC12	60	0	40	1.00	30	125	82.7	3.2
BC13	60	0	40	0.50	3	57	74.0	5.5
BC14	60	0	40	0.50	15	98	88.8	6.6
BC15	60	0	40	0.50	30	125	89.6	9.5