

SUPPLEMENTARY INFORMATION:

Application of microfluidics to control product selectivity during non-catalytic oxidation of naphthenic-aromatic hydrocarbons

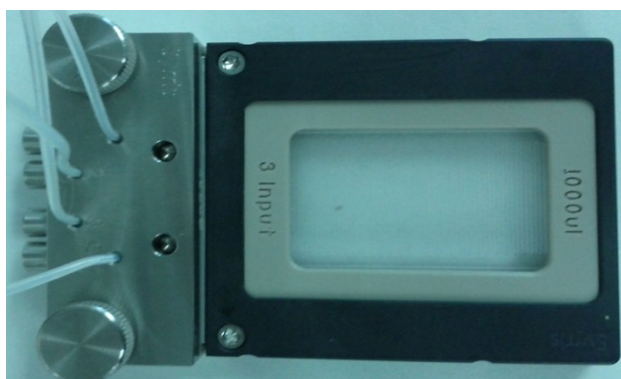
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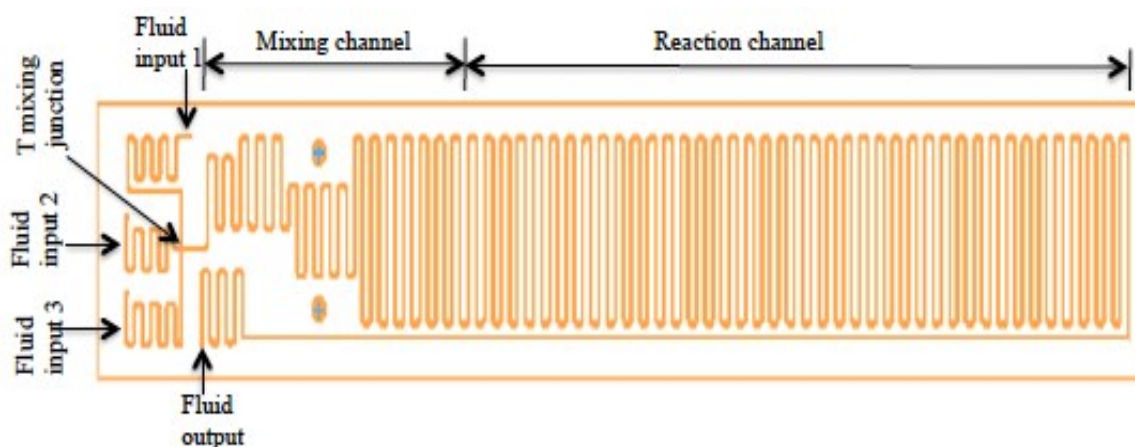
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1. Microfluidic Reactor

A glass microfluidic reactor was used in this study is shown in [Figure S1](#). The reactor volume was 1000 μl having a mixing channel of depth=1240 μm , width= 161 μm , length= 536 mm and a reaction channel of depth=1240 μm , width= 391 μm , length= 1844 mm). It had three inlet ports and one outlet port. Oxygen and tetralin were injected into the reactor using fluid input 1 and fluid input port 2, respectively, and port 3 was blocked.



(a)



(b)

Figure S1. Microfluidic reactor (a) used in tetralin oxidation and its sketch (b).

2. Flame Ionization Detector (FID) Response Factors

The flame ionization detector (FID) has different responses to various organic compounds. So, it is required to calculate response factors for accurate quantification of oxidative conversion by GC-FID. The Dietz-method ⁽¹⁾ was used to calculate the response factors:

$$\text{Response factor (RF)}_{\text{Dietz}} = \frac{(\text{area of compound})(\text{mass of standard})}{(\text{mass of compound})(\text{area of standard})}$$

Heptane was used as the standard and its response factor was 1.00. The calculated relative response factors are tabulated in [Table S1](#). The calculated relative response factors are very close the response factors reported in literature.⁽¹⁾⁽²⁾⁽³⁾ The FID response factors previously reported in literature are also listed in [Table S1](#) for comparison.

Table S1. FID response factors of various compounds

Compound Name	Retention Time (minute)	Response factor (RF)	Reported RF value
Heptane	1.72	1.00 ± 0.00	1.00 ⁽¹⁾
CHCl ₃	1.52	0.09 ± 0.01	
Hexachlorobenzene	8.67	0.32 ± 0.01	0.31 ⁽²⁾
Tetralin	4.90	1.08 ± 0.01	1.02 ⁽³⁾
1,2,3,4-tetrahydro-1-naphthol	6.35	0.82 ± 0.02	
alpha-tetralone	6.51	0.84 ± 0.01	0.80 ⁽³⁾

3. Conversion Calculations

Conversion was calculated based on the tetralin disappearance and did not reflect the extent of oxidation. The percentage conversion was calculated as follows:⁽⁴⁾

$$W_i = \frac{A_i * W_{HCB}}{A_{HCB} * RRF_{i,HCB}}$$

Where, $RRF_{i,HCB} = \frac{RF_i}{RF_{HCB}}$

= Relative response factor of model compounds with respect to hexachlorobenzene (internal standard)

RF_{HCB} = Response factor of hexachlorobenzene with respect to heptane

RF_i = Response factor of model compound with respect to heptane

W_i = Weight % of model compounds

W_{HCB} = Weight % of hexachlorobenzene

A_i = Peak area of model compounds

A_{HCB} = Peak area of hexachlorobenzene

For the conversion less than 1 (wt/wt %), the tetralin conversion was calculated based on the formation of products. A conversion factor was calculated using the data obtained from oxidation of tetralin with air conducted in a semi-batch reactor (Table S2).⁽⁴⁾ Conversion factor was multiplied by sum of relative peak areas of product area to get the conversion. Conversion factor was selected based on the sum of product area.

Table S2. Conversion data for oxidation of tetralin with air at 130 °C conducted in a semi-batch reactor.⁽⁴⁾

Time	conversion	sum of oxidized products	conversion factor
30 min	0.8	214.8	0.0035
1 hr	1.1	643.3	0.0017
2 hr	2.1	1128.1	0.0019
4 hr	4.5	2922.5	0.0015
6 hr	6.9	4628.7	0.0015

Conversion rate was calculated by multiplying conversion with molar flowrate.

4. Diffusion Coefficient Calculation

Different correlations are available in literature to calculate the diffusivities in liquid. Correlation provided by Díaz et al. (1987) can be used to calculate diffusivity of gases in liquid over wide temperature range.⁽⁵⁾ This correlation is used to calculate the diffusion coefficient of oxygen in tetralin (D_A) at 150 °C.

Díaz et al. Correlation: ⁽⁵⁾

$$(D_A)_T = 4.996 \times 10^3 (D_{AB})_{T=25^\circ\text{C}} e^{(-2539/T)}$$

$$(D_A)_{T=25^\circ\text{C}} = 6.02 \times 10^{-5} \frac{V_B^{0.36}}{\mu_B^{0.61} V_A^{0.64}}$$

Where,

$(D_A)_T$ is the diffusion coefficient of oxygen in tetralin at given temperature in cm^2/s

$(D_A)_{T=25^\circ\text{C}}$ is the diffusion coefficient of oxygen in tetralin at 25 °C in cm^2/s

T is the absolute temperature (K) = 423 K

μ_B is the viscosity of tetralin = 2 cp

V_A is the molar volume of oxygen at the normal boiling point temperature (cm^3/gmol) = 27.9 cm^3/gmol

V_B is the molar volume of tetralin at the normal boiling point temperature (cm^3/gmol) = 135.7 cm^3/gmol

$$(D_A)_{T=25^\circ\text{C}} = 2.7 \times 10^{-09} \text{ m}^2/\text{s}$$

$$(D_A)_{T=150^\circ\text{C}} = 3.4 \times 10^{-08} \text{ m}^2/\text{s}$$

5. Physicochemical Properties of Tetralin and Oxygen

Physicochemical properties of tetralin and oxygen used for the calculation shown in the study are listed [Table S3](#). Most of the properties are interpolated from the values obtained from the reported literatures.

Table S3. Physicochemical properties of tetralin and oxygen at different experimental conditions

Temperature (°C)	Tetralin				Oxygen			
	density ⁽⁶⁾ (kg/m ³)	surface tension ^{a (8)(9)} (N/m)	dynamic viscosity ⁽⁶⁾ (Pa.s)	kinematic viscosity ⁽⁶⁾ (m ² /s)	dynamic viscosity ⁽⁷⁾ (Pa.s)	density ^b (kg/m ³)	kinematic viscosity ⁽⁷⁾ (m ² /s)	D _A ⁽⁵⁾ (m ² /s)
25	9.66E+02	3.51E-02	1.17E-03	1.21E-06	2.15E-05	2.36E+00	9.08E-06	2.73E-09
120	8.87E+02	2.57E-02	6.36E-04	7.17E-07	2.59E-05	1.79E+00	1.44E-05	2.14E-08
130	8.79E+02	2.48E-02	5.84E-04	6.65E-07	2.64E-05	1.75E+00	1.51E-05	2.52E-08
140	8.71E+02	2.38E-02	5.33E-04	6.13E-07	2.68E-05	1.71E+00	1.57E-05	2.93E-08
150	8.62E+02	2.28E-02	4.83E-04	5.61E-07	2.73E-05	1.67E+00	1.64E-05	3.39E-08
160	8.54E+02	2.18E-02	4.34E-04	5.08E-07	2.78E-05	1.63E+00	1.71E-05	3.90E-08

^a with respect to air.

^b density of oxygen was calculated at experimental pressure using ideal gas law.

6. Oxidation of Tetralin in Batch Reactor

The setup of batch reactor is shown in [Figure S2](#). Oxidation process has been described in main manuscript (in Experimental section)

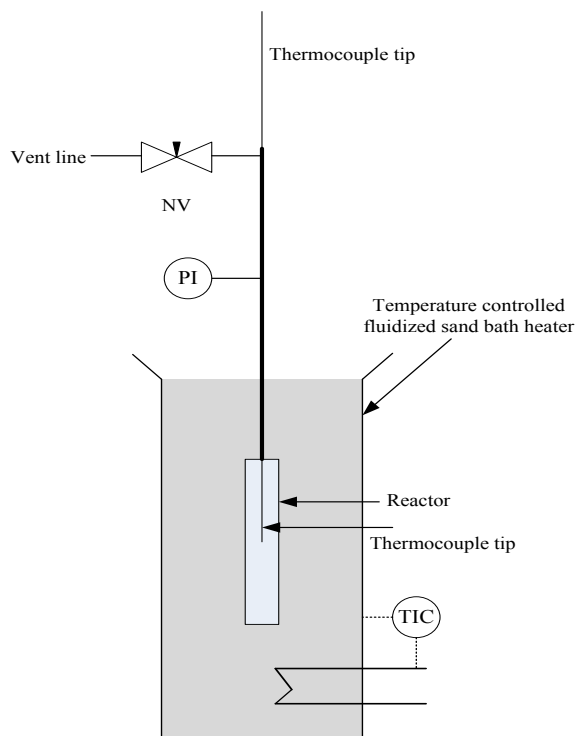
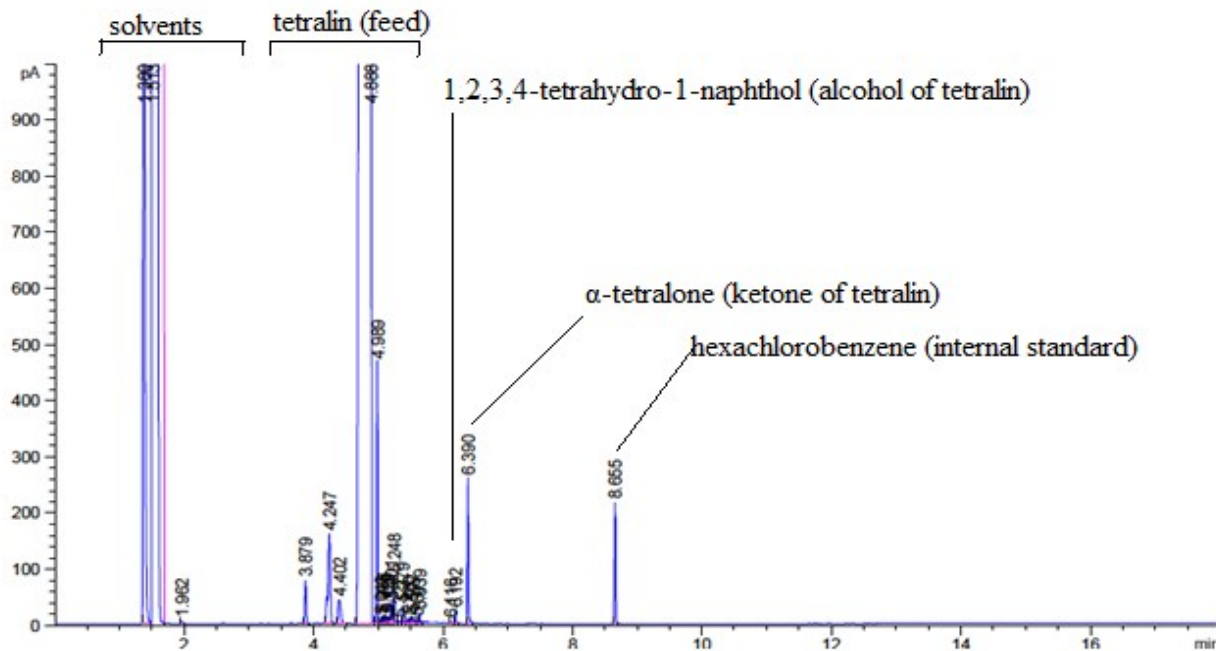


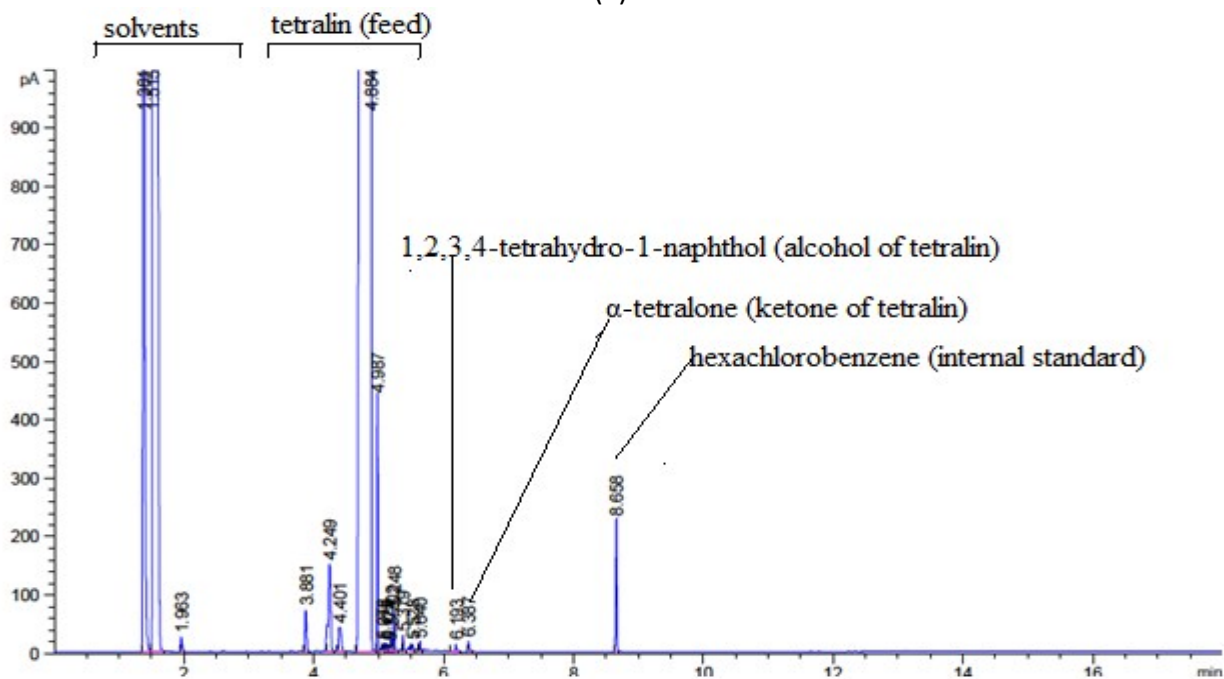
Figure S2. Batch reactor setup used in oxidation experiments.

7. Product identification

GC-FID chromatograms of tetralin oxidized at 150 °C in a microfluidic reactor are shown in Figure S3 to illustrate the ketone-to-alcohol selectivity in primary oxidation product.



(a)



(b)

Figure S3. GC-FID chromatogram of tetralin oxidized at 150 °C in a microfluidic reactor at gas-liquid interfacial area: (a) $3 \times 10^5 \text{ m}^2/\text{m}^3$ (Series A) and (b) $5 \times 10^3 \text{ m}^2/\text{m}^3$ (Series E).

8. Conversion and Product Selectivity during Autoxidation of tetralin in Semi-Batch Reactor

Table S4 shows conversion and selectivity of tetralin oxidized in a semi-batch reactor at 130 °C and atmospheric pressure using air as oxidizing agent.⁽⁴⁾

Table S4. Conversion and selectivity of tetralin oxidized in a semi-batch reactor at 130 °C and atmospheric pressure using air as oxidizing agent.⁽⁴⁾

oxidation time (h)	tetralin conversion (wt%) ^{a (4)}	selectivity of oxidation products (wt %) ^{a,b (4)}			ketone to alcohol in primary oxidation products ^{a, c}
		Primary	Secondary	Addition	
0.5	0.8	100	0	0	1.76
1	1.1	99	1	0	2.58
2	2.1	95	5	0	2.55
4	4.4	86	7	5	1.58
6	6.9	84	5	11	0.90

^a average of two runs

^b weight percentage of all oxidized products in the liquid

^c not reported in ⁽⁴⁾

9. Thermal analysis of di-tert-butyl peroxide (initiator)

Typical DSC (differential scanning calorimeter) curves of di-tert-butyl peroxide obtained at different heating rates under N₂ atmosphere are shown in [Figure S4](#).

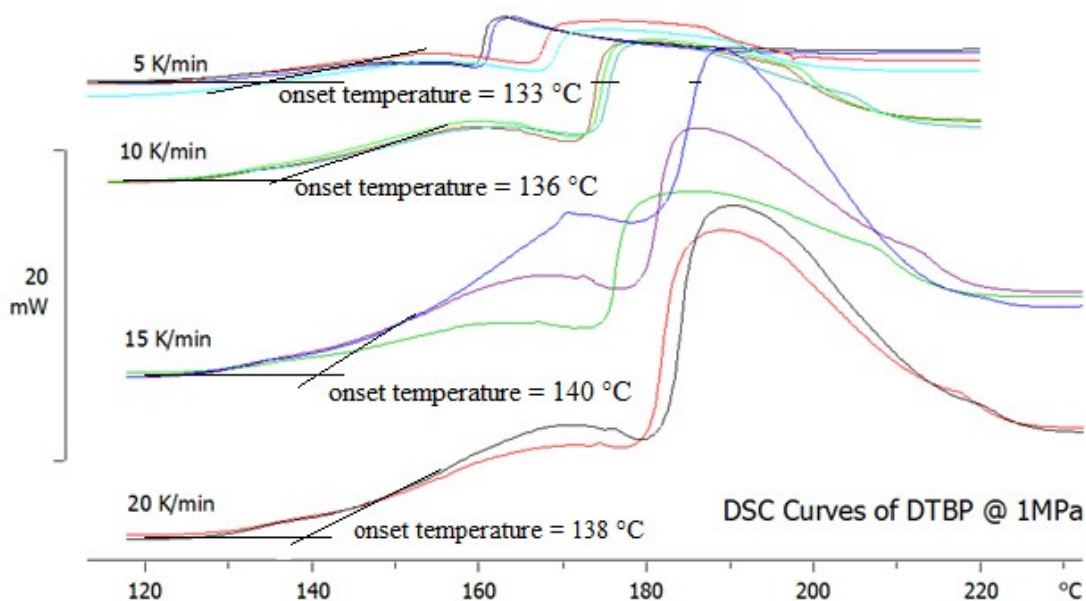


Figure S4. Typical DSC (differential scanning calorimeter) curves of di-tert-butyl peroxide obtained at heating rate of 5-20 °C/min from 25 to 220 (or 230) °C under N₂ atmosphere.

10. Calculation of mass transfer coefficient based on penetration theory

Overall volumetric mass transfer coefficient can be calculated reported by Vandu et al. (2005):¹⁰

$$k_L a = k_{L, cap} a_{cap} + k_{L, film} a_{film}$$

$k_{L, cap}$ and $k_{L, film}$ can be estimated based on penetration mass transfer model as reported by Vandu et al. (2005):¹⁰

$$k_{L, cap} = 2 \sqrt{\frac{2DV_b}{\pi^2 d_c}} \text{ and } k_{L, film} = 2 \sqrt{\frac{D}{\pi t_{film}}}$$

Where, t_{film} is the contact time of the liquid film with the gas bubble, V_b is the bubble rise velocity, D is the liquid phase diffusivity, d_c is the capillary inner diameter.

11. Literature Cited

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