*Catalytic gasification of algae in supercritical water for biofuel production and carbon capture*

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**Electronic Supplementary Information**

**Supplementary Methods**

*High pressure batch reactor system and gas analysis*

The high-pressure sections of the reactors were constructed with standard parts from HiP (High Pressure Equipment Company, USA). The reactor consisted of a high-pressure 316 stainless steel tube (25.4 mm o.d. × 14.3 mm i.d., length 152.4 mm). A sheathed 1.6 mm K-type thermocouple was fitted to the bottom, in contact with the fluid inside the reactor. Additionally, a second K-type thermocouple measured the outside reactor wall temperature at the top of the reactor, in order to detect temperature gradients over the reactor. A 316 stainless steel capillary tube (length 223 mm, 3.2 mm o.d. × 1.6 mm i.d.) was connected to the reactor tube by a high-pressure union, thus connecting the hot part of the reactor with the cold upper part and the gas sampling system. The gas sampling system consisted of two high pressure valves in sequence. Gas samples could be taken with a gas sampling bag (volume 1 L, SKC). The gas samples were analyzed off-line with the help of a gas chromatograph (Agilent 6890). Helium (99.999 vol%) was used as the carrier gas at a flow rate of 11.5 ml/min. The GC was equipped with a Thermal Conductivity Detector (TCD) heated to 250°C and a two column switching system (HP-Plot Q, 30 m x 0.53 mm x 40 µm film thickness, and HP-Plot Molecular Sieve 5A, 30 m x 0.53 m x 50 µm film thickness). Hydrocarbons were measured with a Flame Ionization Detector (FID, heated to 250°C, $H_2$ flow 35 ml/min., air flow 350 ml/min., Helium flow 55 ml/min.). The gas chromatograph was calibrated with three different calibration gases as shown in Table 1. All the gas samples were injected manually with a 250 µl gas-tight syringe (SGE, Australia).

Carbon monoxide, carbon dioxide, methane, nitrogen, and argon were well detected by the TCD. However, hydrogen at low concentrations was not well detected due to the small difference in thermal conductivity between hydrogen and the carrier gas helium. The lower detection limit was ca. 1 vol % for hydrogen. Gas compositions are given on an argon-free basis, and the sum of all measured gases is scaled to 100 vol%.

*Catalyst preparation & characterization*

A commercial 2 wt% ruthenium on granular coconut carbon catalyst (Sample Code: 44915, Lot: 11829) was obtained from Engelhard-BASF (Italy). Characterization of the fresh 2% Ru/C catalyst has been described in detail by Waldner[1].

A 2 wt% Ru/ZrO$_2$ catalyst was prepared in-house by mixing 15 grams of ZrO$_2$ (Daiichi Kigensko Kagaku Koyo Co., LTD) with a particle size between 125-250 μm with 20 ml Ru(NO)(NO$_3$)$_3$ (Alfa Aesar, Ruthenium (III) nitrosylnitrate solution Ru 1.5 % w/v) in an Erlenmeyer flask. The mixture was allowed to rest overnight and the liquid was subsequently evaporated from the mixture for about 2 h at 80°C and 120 torr with a Rotavapor (Büchi RE 111). Finally, the catalyst was calcined in air at 350°C for 3 hours. The BET surface area of the as-prepared catalyst (determined with an Autosorb-1 from Quantachrome Instruments) was 76 m$^2$/g.

*Biomass source & characterization*

*Spirulina platensis* was obtained as a fine powder from a commercial food supplier (Josefs NaturBiokraft, Hasle, Switzerland). The food grade microalgae (BAG-N-Nr. 50511, PharmaCode 2219895, Art.I-Nr. Spp00125) contained less than 3 wt% of water. Before each experiment the microalgae were dried for 1 hour at 105°C in a drying oven (Mettler PM100 combined with a Mettler LP16).

The elemental composition of *Spirulina platensis* was determined at ETH Zurich (Laboratory for Organic Chemistry). The calibration substance for CHN analysis was acetanilide. The following analyzers were used: carbon: LECO CHN-900, oxygen: LECO RO-478, sulphur: LECO CHNS-932.

The ash content was determined in duplicate at 550°C for 1 h in a furnace (Nabertherm C6D), cooled down in a desiccator to balance temperature, weighed and again treated at 550°C for 30 min until the change in weight was less than 4% or 50 mg, according to ref. 2, method 2540 G.

*Liquid sample analysis*

Liquid samples were obtained through filtration of the batch reactor content over a membrane filter (regenerated cellulose, pore size 0.45 μm, dia. 47 mm, Schleicher & Schuell Microscience GmbH, Dassel, Germany) with a vacuum filtration apparatus from Sartorius (Goettingen, Germany). Nonpurgeable organic carbon (NPOC) was measured on a TOC – Vwp (Total Organic Carbon Analyzer) from Shimadzu connected to an ASI-V autosampler (also from Shimadzu). The NPOC was measured by the persulphate/UV oxidation method at 80°C. Standards for the NPOC analysis were prepared from potassium hydrogen phthalate salt (FLUKA) and pure water from a Milli-Q station (Millipore). The pH of the aqueous samples was measured with color-fixed pH indicator sticks (pH 7-14, Fisherbrand, EU Code: FB33015).

*Calculation of the amount of gasified feed carbon, the C1-C3 yield, and the estimation of uncertainty*

The yield of methane, ethane, and propane ($Y_{C1-C3}$) was calculated based on the results of the gas analysis. To take into account uncertainties in ambient pressure ($\Delta p$), total gas volume determination ($\Delta V$) and volume fraction of $C_1$-$C_3$ in the product gas ($\Delta X$), an error calculation was done. $\Delta p$ and $\Delta V$ are constant values derived from experience. $\Delta X$ was derived from the standard deviation obtained from the GC analysis of the product gas.

$$Y_{C1-C3} = m_{C1-C3} / m_{DM} = f(V, p, X)$$
$$m_{C1-C3} = m(CH_4) + m(C_2H_6) + m(C_3H_8)$$
$$\Delta m_{C1-C3} = \left| \frac{(\partial m_{C1-C3})}{\partial V} * \Delta V \right| + \left| \frac{(\partial m_{C1-C3})}{\partial p} * \Delta p \right| + \left| \frac{(\partial m_{C1-C3})}{\partial X} * \Delta X \right|$$
$$\Delta Y_{C1-C3} = \Delta m_{C1-C3} / m_{DM}$$

$V$ = Volume of gas sampling bag ($m^3$).

$p$ = ambient atmospheric pressure (hPa).

$X$ = percentage of $CH_4$ + $C_2H_6$ + $C_3H_8$ in the product gas (vol%) obtained from GC measurements.

$\Delta p$ = 2 hPa; $\Delta V$ = $10^{-5}$ $m^3$; $\Delta X$ = $\sigma_{C1-C3}$ *(vol %)*. The standard deviation $\sigma_{C1-C3}$ ranged from 0.2 % up to 11.3 %.

The amount of gasified feed carbon was calculated by the following formula:

$$C_{gas} / C_{feed} = m(C_{gas}) / m(C_{feed}) \times 100\%$$

With m($C_{gas}$) representing the carbon content of the product gas:

$$m(C_{gas}) = \left( mol_{CO_2gas} + mol_{CO_2dissolved} + mol_{COgas} + mol_{CH_4gas} + 2 * mol_{C_2H_6gas} + 3 * mol_{C_3H_8gas} \right) * 12.01 g / mol_{Carbon}$$
$$m(C_{feed}) = m_{DM} * w_C$$

$mol_{CO2gas}$=$CO_2$ content in the product gas (mol)

$mol_{CO2dissolved}$= dissolved $CO_2$ content in the liquid fraction (mol)

$mol_{COgas}$=CO content in the product gas (mol)

$mol_{CH4gas}$=$CH_4$ content in the product gas (mol)

$mol_{C2H6gas}$=$C_2H_6$ content in the product gas (mol)

$mol_{C3H8gas}$=$C_3H_8$ content in the product gas (mol)

$w_C$ = 0.478 (carbon mass fraction in the dried *Spirulina p.*).

The parameter $mol_{CO2dissolved}$ is strongly affected by the measured pH in the liquid effluent of the reactor, because the solubility of $CO_2$ is a strong function of the pH. As our batch reactor is a non-stirred system, a considerable uncertainty about how much of the $CO_2$ is dissolved in the liquid phase exists.

**References**

1.  M. H. Waldner, PhD thesis, ETH Zürich, Switzerland, 2007.

2.  A. D. Eaton, et al., ed., Standard Methods for the examination of water and wastewater, APHA, Washington, DC, USA, 21st edn., 2005.

**Supplementary Tables**

**Table 1** Gas mixtures used for GC calibration

| Component | Mixture 1 vol % | Mixture 2 vol % | Mixture 3 vol % | Retention time TCD (min.) | Retention time FID (min.) |
|---|---|---|---|---|---|
| $CH_4$ | 10 | 2 | 91 | 5.6 | 2.7 |
| $C_2H_6$ | - | - | 7 | n.d. | 2.9 |
| $C_3H_8$ | - | - | 2 | n.d. | 3 |
| CO | 5 | 3 | - | 7 | n.d. |
| $CO_2$ | 10 | 20 | - | 2.5 | n.d. |
| $H_2$ | 10 | 42 | - | 3.8 | n.d. |
| Ar | 65 | - | - | 4.1 | n.d. |
| $N_2$ | - | 33 | - | 5 | n.d. |

N.d.: not detected