

# HORIZON-CL5-2022-D3-03-07

## SUSTAINABLE JET FUELS FROM CO<sub>2</sub> BY MICRO-ALGAL CELL FACTORIES IN A ZERO WASTE APPROACH

# ALFAFUELS

### D5.1 - Method for isoprene assessment /recovery from PBR

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# 1. Executive summary

Biological production routes of isoprene -such as engineered cyanobacteria or algae- offer carbon-neutral synthesis from CO<sub>2</sub> and sunlight, but the downstream separation of isoprene from humid off-gas streams remains a practical bottleneck, especially at low gas concentrations.

Isoprene's boiling point of 34 °C and vapour pressure of ~70 kPa at 25 °C make it highly volatile and only weakly soluble in water (Henry's law constant 0.013-0.028 mol·kg<sup>-1</sup>·bar<sup>-1</sup> at 25 °C; solubility ≈600 mg·L<sup>-1</sup>). Therefore, recovery based on adsorption, absorption or condensation from isoprene produced in aqueous media is thermodynamically well-motivated, since the equilibrium strongly favours the gas phase over dissolution in water.

This report compares fundamental routes for capturing and releasing isoprene from bioreactor off-gas streams, with emphasis on two scalable, cost-effective strategies: (1) sorption on porous solids (hydrophobic silica gel; Carbopack-type carbons as analytical references), and (2) condensation-based capture, including Temperature-Swing Condensation (TSC) and Liquid Absorption Capture (LAC) using PDMS as a low-cost alternative to commercial long-chain alkane solvents.

These approaches build on patent literature (WO2011075534 A2, EP2980221 A1)<sup>6,7</sup> which describe solvent scrubbing with hydrocarbons and cryogenic condensation and explore low-temperature desorption (30–40 °C) without stripping gas as a route to avoid product dilution and potentially improve energy efficiency for small to medium scale bioreactor integration.

Together, the strategies span the main thermodynamic mechanisms available for ppm-level hydrocarbon recovery and offer practical pathways for renewable isoprene production.

A critical consideration – now explicitly addressed – is aqueous phase partitioning via Henry's law, which significantly affects off-gas quantification during calibration and measurement, and also constrains gas-flow design for efficient isoprene stripping while managing co-evolved oxygen.

## 2. Acronyms and abbreviations

<b>Abbreviation</b>	<b>Definition</b>	<b>Context</b>
$A_{solv}$	Peak areas from GC-FID-data for solvent, reference etc.	Used for recovery efficiency calculations
$A'_{solv}$	Fitted slopes from $A_{solv}$ , $A_{ref}$ etc.	Used for recovery efficiency calculations at time $t$
$C_{aq}$	Aqueous concentration ( $\text{mol}\cdot\text{L}^{-1}$ or $\text{mg}\cdot\text{L}^{-1}$ )	Henry's law calculations
$C_i$ , $C_{ppm}$	Isoprene concentration in gas phase (ppm)	Off-gas measurements
$\text{CO}_2$	Carbon dioxide	Bioreactor input/photosynthesis
$d(\ln k_H)/d(1/T)$	Temperature sensitivity of Henry's law constant	Thermodynamic parameter
$\Delta H_{vap}$	Heat of vaporization	Thermodynamic property, $\sim 25 \text{ kJ}\cdot\text{mol}^{-1}$ for isoprene
<b>FID</b>	Flame Ionization Detector	GC detection method
<b>GC</b>	Gas Chromatography	Offline analytical confirmation
<b>GC-FID</b>	Gas Chromatography with Flame Ionization Detection	Quantitative analysis of desorbed isoprene
<b>GC-MS</b>	Gas Chromatography with Mass Spectrometry	Identity confirmation ( $m/z$ 67 for isoprene)

<b>H350</b>	<i>1,2-dibenzyl-3-methylbenzene, high boiling solvent</i>	<i>CAS: 258-649-2 Liquid absorbent</i>
<b>HL60</b>	<i>Trade name for PDMS silicon oil</i>	<i>Liquid absorbent; low vapor pressure, good isoprene solubility</i>
<b>Hz</b>	<i>Hertz (samples per second)</i>	<i>Data logging frequency</i>
<b>ID</b>	<i>Inner Diameter</i>	<i>Equipment specification</i>
<b>ICP, ICT</b>	<i>Ion Chromatography or Ion Trap Mass Spec (context-dependent)</i>	<i>Analytical methods</i>
<b>K<sub>H</sub></b>	<i>Henry's law constant (mol·kg<sup>-1</sup>·bar<sup>-1</sup>, or mol·L<sup>-1</sup>·bar<sup>-1</sup>)</i>	<i>Solubility parameter can also describe surface loading parameter</i>
<b>L/G</b>	<i>Liquid-to-gas ratio</i>	<i>Absorption design parameter</i>
<b>LAC</b>	<i>Liquid Absorption Capture</i>	<i>Capture method; solvent-based</i>
<b>mbar</b>	<i>Millibar (unit of pressure)</i>	<i>Vacuum/pressure specification</i>
<b>M<sub>iso</sub></b>	<i>Molar mass of isoprene (68.12 g·mol<sup>-1</sup>)</i>	<i>Stoichiometric conversion</i>
<b>mmHg</b>	<i>Millimeters of mercury (pressure unit)</i>	<i>Vapor pressure scales</i>
<b>MS</b>	<i>Mass Spectrometry</i>	<i>Detection method</i>
<b>m<sub>des</sub>, m<sub>in</sub></b>	<i>Mass desorbed / Mass input</i>	<i>Recovery calculation</i>
<b>NIST</b>	<i>National Institute of Standards and Technology</i>	<i>Reference data source</i>

<b>NmL/min</b>	<i>Normal mL per minute</i>	<i>A gas flow normalized to atmospheric pressure</i>
<b>O<sub>2</sub></b>	<i>Oxygen</i>	<i>Co-evolved in photosynthesis (~5 mol per mol isoprene)</i>
<b>p<sub>i</sub>, p<sub>iso</sub></b>	<i>Partial pressure of isoprene or component i</i>	<i>Thermodynamic quantity</i>
<b>P<sub>sat</sub></b>	<i>Saturation vapor pressure</i>	<i>Condensation threshold</i>
<b>P<sub>tot</sub></b>	<i>Total system pressure (typically 1 atm ≈ 1.013 bar)</i>	<i>Reference condition</i>
<b>PDMS</b>	<i>High boiling solvent, polydimethylsiloxane</i>	<i>Liquid absorbent; low vapor pressure, good isoprene solubility</i>
<b>P&amp;ID</b>	<i>Piping and Instrumentation Diagram</i>	<i>Process flowsheet notation</i>
<b>PID</b>	<i>Photoionization Detector</i>	<i>Real-time gas analyzer (10.6 eV UV lamp)</i>
<b>PSD</b>	<i>Pressure-Swing Desorption</i>	<i>Vacuum-based desorption technique</i>
<b>q</b>	<i>Adsorbed loading (mol·g<sup>-1</sup>)</i>	<i>Sorption equilibrium</i>
<b>q<sub>max</sub></b>	<i>Maximum adsorption capacity</i>	<i>Langmuir isotherm parameter</i>
<b>Q<sub>bleed</sub></b>	<i>Bleed stream gas flow rate</i>	<i>Side-stream removal for capture</i>
<b>Q<sub>gas</sub></b>	<i>Total gas flow (L·min<sup>-1</sup>)</i>	<i>Bioreactor aeration/sparge rate</i>
<b>RH</b>	<i>Relative Humidity (%)</i>	<i>Off-gas saturation with water vapor</i>

<b>R</b>	<i>Recovery (fraction or %)</i>	<i>Desorption efficiency: <math>m_{des} / m_{in}</math></i>
<b>T</b>	<i>Temperature (°C or K)</i>	<i>Operating condition</i>
<b>T<sub>dew</sub></b>	<i>Dew point temperature (°C)</i>	<i>Condensation temperature at given ppm</i>
<b>TD, TDS</b>	<i>Thermal Desorption or Thermal Desorption System</i>	<i>GC sample introduction</i>
<b>TSD</b>	<i>Temperature-Swing Desorption</i>	<i>Heating-based desorption technique</i>
<b>TSC</b>	<i>Temperature-Swing Condensation</i>	<i>Cooling-based capture without solvents</i>
<b><math>\tau</math></b>	<i>Time constant (s)</i>	<i>Kinetic sorption parameter; exponential approach to equilibrium</i>
<b>UV</b>	<i>Ultraviolet (10.6 eV photon energy in PID)</i>	<i>Ionization mechanism</i>
<b>vvm</b>	<i>Volume of gas per volume of liquid per minute</i>	<i>Specific aeration rate (e.g., 0.25 vvm)</i>
<b>VOC</b>	<i>Volatile Organic Compound</i>	<i>Generic term for organics detected by PID</i>
<b><math>x_i</math></b>	<i>Mole fraction in liquid phase</i>	<i>Absorption equilibrium</i>
<b><math>y_i</math></b>	<i>Mole fraction in gas phase</i>	<i>Gas-phase composition</i>
<b><math>\eta_c</math></b>	<i>Condensation efficiency (fraction or %)</i>	<i>Removal rate: <math>1 - (C_{out} / C_{in})</math></i>

### 3. Introduction

Deliverable D5.1, “Method for isoprene assessment/recovery from photobioreactor (PBR)”, is the main outcome of subtask 5.1.2 “Design of separation system for pilot scale” and provides the thermodynamic and process basis for recovering isoprene from photobioreactor off-gas under ALFAFUELS conditions. The focus is on methods relevant for TRL5 reactors that can later be assembled into an integrated separation system, to be engineered and demonstrated in WP5 and reported at M30.

D5.1 targets a quantitative model that links bioreactor productivity, gas-flow conditions and off-gas composition to the performance of candidate capture and regeneration steps. This model is meant to support the design of the isoprene recovery system by defining realistic boundary conditions and design envelopes for gas handling, stripping intensity and capture efficiency.

Three complementary separation mechanisms are herein examined: pressure-swing (related to solid sorbents), temperature-swing operations including Temperature-Swing Condensation (TSC), and a solvent cold trap implemented as Liquid Absorption Capture (LAC) with different high-boiling solvent. These techniques are considered both as analytical tools for accurate isoprene quantification and as building blocks for implementation around TRL5 photobioreactors.

The experimental work establishes benchmark capture and desorption behaviour for representative adsorbents and solvents, while the gas-flow and stripping analysis links these data to realistic PBR operating windows (off-gas ppm, aeration rates, bleed-stream concepts). Rather than prescribing a single configuration, D5.1 delineates a set of capture options and operating ranges that can be combined with WP6 photobioreactor design and WP7 upscaling studies. In this way, the deliverable provides a method and data set that can be reused in model-based design of the isoprene recovery system from lab scale to ALFAFUELS pilot reactors.

### 3.1. Photobioreactor context and isoprene production

The photobioreactor used in this project (WP1, Uppsala University) achieves isoprene productivity of up to **6 mg·L<sup>-1</sup>·h<sup>-1</sup>**. Based on current strain optimization, small-scale experiments report carbon partitioning into isoprene of approximately **23%**, meaning that roughly one-quarter of fixed CO<sub>2</sub> is routed into isoprene, while the remainder goes to biomass, maintenance, and other metabolites.<sup>1</sup>

At a typical gas sparge rate of **0.25 L·min<sup>-1</sup> per litre of culture** ( $\approx 0.25$  vvm), the steady-state isoprene concentration in the off-gas is approximately **140-150 ppm** (v/v), as confirmed by mass balance and ideal-gas calculations (Appendix A).

*Table 3.1. Reactor scaling and expected isoprene concentrations*

Reactor Volume	Productivity	Gas Flow	Expected C <sub>iso</sub>
1 L	6 mg·L <sup>-1</sup> ·h <sup>-1</sup>	0.25 L·min <sup>-1</sup>	~144 ppm
12 L	6 mg·L <sup>-1</sup> ·h <sup>-1</sup>	3.0 L·min <sup>-1</sup>	~144 ppm
100 L	6 mg·L <sup>-1</sup> ·h <sup>-1</sup>	25 L·min <sup>-1</sup>	~144 ppm

Thus, laboratory experiments conducted at 100-150 ppm represent a biologically realistic concentration regime. The off-gas composition in a real reactor consists mainly of N<sub>2</sub> or air, with 3-4% CO<sub>2</sub> and saturated water vapour. These conditions were reproduced in the bench-scale system used for all capture and desorption tests.

Cyanobacteria such as *Synechocystis* sp. PCC 6803 are continuously exposed to molecular oxygen as a direct consequence of oxygenic photosynthesis. Elevated oxygen levels can, under certain conditions, contribute to oxidative stress through the formation of reactive oxygen species (ROS), particularly when high light intensities coincide with limited availability of electron sinks such as CO<sub>2</sub> fixation. This phenomenon has been extensively described in the literature and is generally associated with photoinhibition and redox imbalance rather than with oxygen toxicity per se.<sup>2</sup>

However, under conditions where CO<sub>2</sub> is actively supplied and gas exchange is sufficient, oxygen does not typically reach biologically inhibitory concentrations in photobioreactors.<sup>3</sup> Likewise, isoprene is a volatile and

weakly water-soluble compound that rapidly partitions into the gas phase, limiting its accumulation in the culture medium. Reported inhibitory effects of isoprene occur at concentrations several orders of magnitude higher than those expected under continuous stripping and ppm-level gas-phase operation.<sup>4</sup>

Based on these considerations, it is therefore unlikely that isoprene- or oxygen production constitute the primary growth- or productivity-limiting factors under the investigated operating conditions. Process limitations are instead expected to be dominated by metabolic capacity and gas–liquid mass transfer rather than by product or oxygen toxicity.

### 3.2. Adsorption and desorption on porous solids

At low partial pressures, the loading  $q$  ( $\text{mol}\cdot\text{g}^{-1}$ ) follows Henry's adsorption isotherm:

$$q = K_H P_i$$

At higher surface coverage, the Langmuir form applies:

$$q = \frac{q_{\max} b P_i}{1 + b P_i}$$

**Carbon-based adsorbents** (e.g., Carbopack B, graphitised carbon black) exhibit moderate hydrophobicity and adsorption enthalpies of roughly 25–35  $\text{kJ}\cdot\text{mol}^{-1}$  for small hydrocarbons.

**Silica gel adsorbents**, particularly hydrophobic variants (e.g., those treated with dimethyldichlorosilane or octyltriethoxysilane), offer high surface area and tuneable pore structure and are significantly lower cost than graphitized carbon blacks. They are widely used in industrial VOC recovery, and literature indicates that, for non-polar compounds at ppm levels, hydrophobic silica gels can provide:

- Favourable affinity for hydrophobic VOCs
- Reduced water uptake compared with conventional polar silica (important in humid off-gas)
- Regeneration by modest heating (typically 40–100 °C)
- Straightforward scalability to production-scale packed beds.

**Temperature-Swing Desorption (TSD):** Heating increases vapour pressure exponentially. A rise from 25 to 250-350 °C can lower surface coverage by three orders of magnitude. TSD is the basis for standard thermal-desorption analysis in GC-MS.

**Pressure-Swing Desorption (PSD):** Lowering total pressure decreases equilibrium loading. At 10 mbar, a large fraction of weakly bound species can be released even at room temperature; however, most adsorbents typically require vacuum + mild heating (80-120 °C) for efficient recovery.

### 3.3. Condensation and liquid absorption/stripping

**Temperature Swing Condensation (TSC):** Begins when  $P_i \geq P_{\text{sat}}(T)$ . At 1 bar and 150 ppm isoprene,  $T_{\text{dew}} \approx -45$  to  $-50$  °C (from low-temperature Antoine constants, Appendix C). Even though processes at these temperatures are outside the scope of the ALFAFUELS concept (due to high energy costs), partial capture could be feasible at modest cooling (0 to 5 °C) via kinetic/nucleation-driven mechanisms, resulting in higher-than-expected condensation. At these temperatures TSC can also be used for separation of water from humid reactor off-gas before capturing of isoprene.

**Liquid Absorption Capture (LAC):** Isoprene dissolves in water (or other hydrophobic liquids) according to Henry's law with a very small  $K_H$  value, which means that most of the produced isoprene will partition to the gas phase in a bioreactor (see section 4.3). LAC is a separation method based on solvents with much higher partitioning constants  $K$  (defined exactly like Henry's constant but valid at higher concentrations), which therefore can absorb isoprene from the reactor off-gas. In essence isoprene is transferred from a large aqueous volume to a smaller adsorption liquid volume based on the difference in affinity for isoprene. In a final step isoprene can be recovered from the absorption liquid, pure or at high concentrations, by a suitable desorption technique based on changes in temperature and pressure.

### 3.4. Patent context

**Patent precedent and commercial solvents:** WO2011075534 A2 (2011)<sup>6</sup> describes two-stage absorption-stripping systems using long-chain alkane

mixtures, typically C<sub>12</sub>-C<sub>16</sub>, for isoprene recovery from renewable fermentation feedstocks. The patent demonstrates:

- High isoprene loading in hydrocarbon solvents at 25-40 °C
- Efficient regeneration via heating to 60-80 °C combined with inert gas stripping
- Scalability to large industrial installations

**EP2980221 A1**<sup>7</sup> (Japanese patent on isoprene collection, 2016) describes complementary approaches:

- Pure condensation (no solvent) at cryogenic temperatures (below -40 °C)
- Water-based and non-aqueous absorption routes
- Trade-offs between temperature, energy input, and recovery efficiency

### 3.5. Our strategy for ALFAFUELS

Encouraged by the possibility to implement large-scale hydrocarbon loops (requiring heated reboilers, condensers, and distillation), we propose **smaller-scale, modular alternatives suitable for pilot bioreactors and the target TRL5:**

1. **PDMS** as a liquid absorbent - combines moderate solubility, low vapor pressure, and easy thermal regeneration without stripping gas.  
PDMS has previously been identified as a promising material for separating isoprene from biologically derived gas streams, both in membrane form and, in this work, as a liquid absorbent for low-temperature trapping. Membrane-based polishing of isoprene (e.g. using PDMS or polyetherimide membranes) has been demonstrated for similar gas compositions, suggesting that the dilute product streams obtained from the present capture modules could be further upgraded by polymer-membrane separations.<sup>2</sup>
2. Optionally, the solvent absorption can be complemented with a polishing step using **Hydrophobic silica gel** as a solid-phase adsorbent - easily recharged, no moving parts

This approach bridges the gap between laboratory TSC/adsorption and industrial solvent scrubbing, offering practical solutions for medium-scale deployment (10-100 L bioreactors) with clear pathways to larger systems.

### 3.5.1. Low-Temperature Desorption (30-40 °C) without Stripping Gas: Rationale and Design

**Why low-temperature desorption matters for isoprene capture:**

Conventional desorption (TSD, PSD) often requires:

- High temperature (200-350 °C for TSD) or deep vacuum (<10 mbar for PSD)
- Stripping gas (He, N<sub>2</sub>) to carry desorbed vapor into a trap or analysis instrument
- The stripping gas **massively dilutes** recovered isoprene, complicating downstream concentration and use

For a pilot-scale isoprene recovery system, these limitations are significant:

- **TSD equipment cost:** Heating to 200-350 °C requires a furnace or oven with GC interface; energy costs are substantial.
- **Product dilution:** Stripping with on the order of 100-1000 mL of helium or nitrogen dilutes recovered isoprene to low ppm-levels, requiring a demanding second concentration step (e.g., cryogenic trapping, further absorption).
- **Downstream processing:** The photochemistry in ALFAFUELS requires liquid isoprene, not a gas mixture.

## 4. Results and Discussion

### 4.1. Carbopack B Breakthrough Testing: Adsorbent evaluation for pilot-scale capture

#### Background and Methodology

As part of the solid-phase adsorbent evaluation for the ALFAFUELS WP5 capture module, two graphitic carbon adsorbents were tested for their ability to retain isoprene under dynamic gas flow conditions (breakthrough testing). The goal was to establish baseline capacity and scalability parameters for initial dimensioning of a pilot-scale gas trap.

#### Materials Tested

##### Carbopack B (Merck KGaA, Darmstadt, Germany):

- Graphitized carbon black adsorbent
- Mesh size: 60-80
- Nominal surface area: 100 m<sup>2</sup>/g
- Readily available in pre-packed thermal desorption (TD) tubes
- High affinity for isoprene; does not retain significant amounts of water
- **Cost: €80 per gram** (bulk orders of 5-10 g); used for analytical isoprene determination in process gas

##### Activated Charcoal (DARCO, Cabot Norit Americas, Inc):

- Acid-washed lignite-type carbon
- Mesh size: 20-40
- Nominal surface area: 650 m<sup>2</sup>/g (higher than Carbopack B)
- Readily available in bulk at much lower cost than Carbopack B
- TD tubes were manually packed for this study (introduces slightly larger variation between replicates)

#### Breakthrough Volume Testing

**Methodology:** A plug-flow test was conducted where an isoprene gas standard ("challenge load") was introduced at the entrance of the

adsorbent tube. A flow of nitrogen ("challenge volume") was then passed through the tube. The **breakthrough volume** is defined as the total volume of challenge gas (isoprene + N<sub>2</sub>) per gram of adsorbent at which the recovered isoprene (measured by thermal desorption) drops to a defined recovery criterion (typically 90-95% of the initial challenge load). The true saturation capacity of such adsorbents for VOCs is typically 0.1–1 wt%, but under dilute gas-phase conditions breakthrough is almost always reached well before saturation, so dynamic breakthrough volume is the relevant design parameter rather than absolute saturation capacity.

**Key interpretation:** The breakthrough volume reflects how much carrier gas can flow through the bed before it begins to significantly desorb the previously captured isoprene dose. It is a **dynamic measure** of retention robustness, not a measure of saturation with fresh isoprene in the sweep gas (which is nitrogen and contains no isoprene).

### **Results: Carbopack B**

#### **Breakthrough volume at room temperature (22 °C): 120 L/g of adsorbent**

This result indicates that 1 gram of Carbopack B can be exposed to approximately **120 liters** of the isoprene challenge gas stream before the retained isoprene begins to be stripped, dropping below the 90-95% recovery criterion. For Carbopack B, the effective recovery can be treated as 100%, because the loaded mass determined from thermal desorption can be cross-checked against direct injection of the same liquid standard into the GC, making Carbopack B a practical reference sorbent for isoprene in this study.

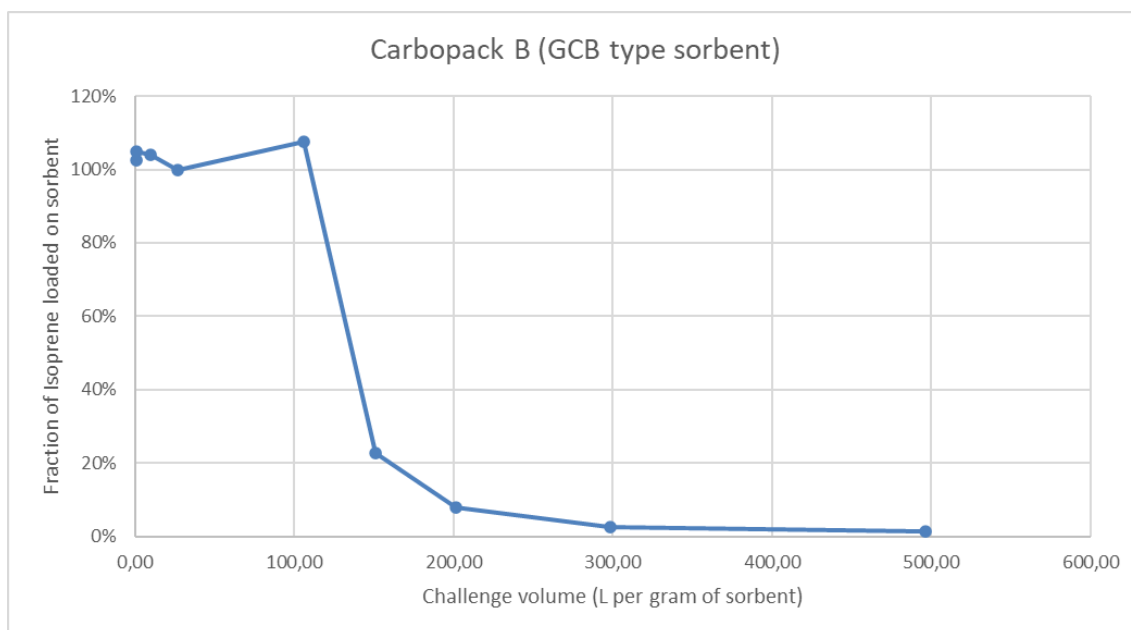


Figure 4.1. Breakthrough curve for isoprene on Carbopack B at 22 °C, showing quantitative retention up to a challenge volume of ~120 L·g<sup>-1</sup>.

Figure 4.1 shows that Carbopack B retains essentially the entire isoprene challenge load up to a challenge volume of roughly 120 L·g<sup>-1</sup> at 22 °C, after which the recovered fraction drops below 90–95%, defining the dynamic breakthrough volume used for scale-up.

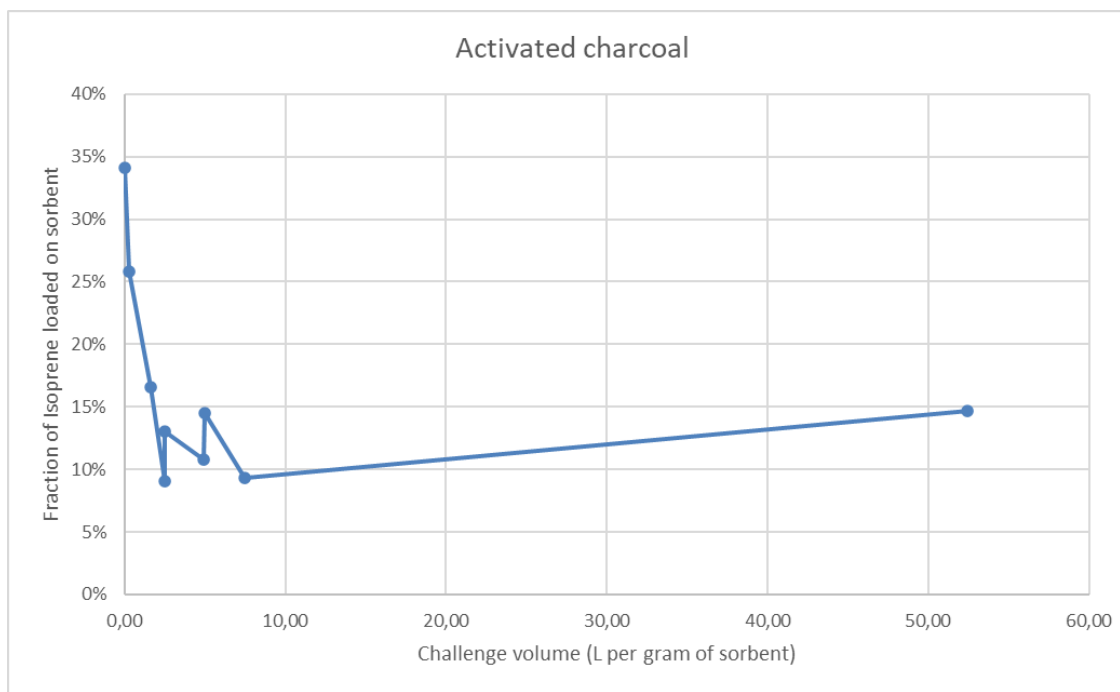
#### Implications for pilot-scale design:

- For a target isoprene concentration of 100-150 ppm in a 10-100 L bioreactor off-gas stream, a Carbopack B bed on the order of **0.1-1 gram** would be expected to have a practical operating life of hours to days before saturation, depending on gas flow rate and exact residence time.
- Scaling to larger beds is feasible if the ratio of bed diameter to bed length (and preferably also the linear gas velocity) is maintained similar to the test conditions.
- The high breakthrough volume and low water retention make Carbopack B an excellent choice for analytical sampling and secondary polishing stages.

**Economic consideration:** At €80 per gram, Carbopack B is prohibitively expensive for a primary bulk capture bed in continuous operation. For a 100 L reactor bleeding 25 L/min of gas (0.25 vvm), a primary adsorbent bed would quickly become cost-prohibitive if based on Carbopack B alone. This

economic constraint motivates the evaluation of **hydrophobic silica gel** (Section 4.2) and **PDMS absorption** (Section 4.6) as lower-cost primary capture options.

## Results: Activated Charcoal



*Figure 4.2. Breakthrough behaviour for isoprene on activated charcoal (DARCO) at 22 °C; the recovered isoprene fraction never exceeds ~35% even at low challenge volumes, suggesting irreversible loss or poor retention under these conditions despite the higher nomina*

The maximum recovered fraction from the activated charcoal tubes never exceeded ~35%, even at very small challenge volumes, and only increased slightly when the gas volume was reduced (Figure 4.2). This shows that breakthrough happens very early, even for millilitre-scale gas loads, and that any irreversibly bound isoprene is a smaller issue than the fundamentally low usable capacity of this specific acid-washed charcoal.

**Breakthrough volume:** Could not be determined accurately; even at very small challenge volumes (mL range), the recovery never exceeded **35% of the challenge load** (Figure 4.2).

**Interpretation:** The high nominal surface area (650 m<sup>2</sup>/g, 6.5× higher than Carbopack B) would normally predict superior adsorption. The poor recovery suggests either:

1. **Irreversible loss** – Isoprene is being chemically reacted or polymerized on the activated charcoal surface, particularly if the

charcoal has residual acidic or reactive functional groups despite the acid-wash treatment.

2. **Poor affinity** – The activation process and resulting pore structure may be optimized for different analytes (e.g., larger molecules or more polar compounds), leaving the Carbopack surface inherently more polar than Carbopack B, which reduces isoprene retention.

**Recommendation:** Activated charcoal is **not recommended as a primary adsorbent** for isoprene capture at this stage. The poor and irreproducible recovery suggests material-specific issues rather than general limitations of activated carbon. Alternative activated carbons or surface-modified variants could potentially perform better, but such testing is outside the current project scope.<sup>8</sup>

The erratic behavior in the 8-15% recovery range (Figure 2) is attributed to variation in manual TD tube packing, which affects gas-solid contact and breakthrough timing.

### **Vacuum Desorption Test (Pressure-Swing Desorption)**

In addition to breakthrough characterization, the feasibility of **pressure-swing desorption (PSD)** was evaluated. The vacuum test (10 mbar, 20 min at room temperature) was designed as a back-diffusion experiment, analogous to passive sampling, to check whether pressure-swing could recover a substantial fraction of the residual isoprene in a reasonable time. The observation that ~26% of the loaded isoprene could be recovered under these conditions indicates that vacuum provides a meaningful driving force for desorption when only ~25% of the mass remains, and suggests that a practical PSD process operated at more moderate pressures (e.g. 100–200 mbar) could significantly reduce gas volume and energy consumption compared with high-temperature TSD.

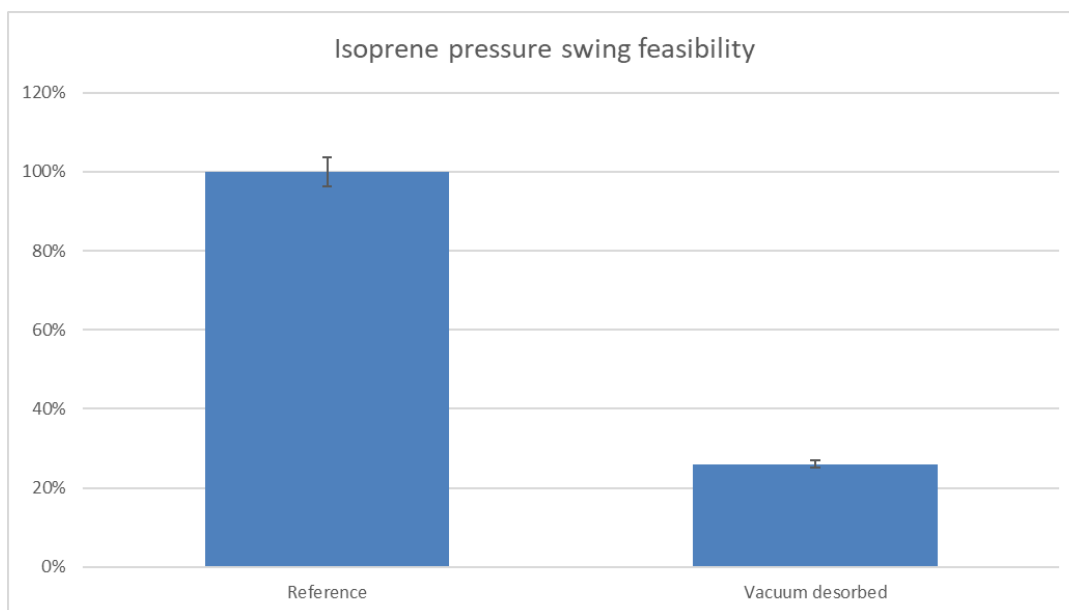


Figure 4.3. Recovery of isoprene from Carbopack B after 20 min exposure to 10 mbar vacuum at room temperature, demonstrating that pressure-swing desorption can release ~26% of the loaded isoprene without heating, but that additional mild heating and/or longer cont

**Result: 26% recovery** after 20 minutes at 10 mbar and 25 °C (Figure 4.3).

**Interpretation:** This demonstrates that isoprene can be partially desorbed from Carbopack B at room temperature under vacuum, showing that the adsorption enthalpy ( $\sim 25\text{-}35 \text{ kJ}\cdot\text{mol}^{-1}$  for graphitized carbon black) is modest enough to permit non-thermal desorption. However, 26% recovery is insufficient for practical single-stage desorption. In practice:

- **Combining vacuum with mild heating (80-100 °C)** would be necessary to approach TSD-level recovery (90-100%) at significantly lower total energy than TSD alone.
- Alternatively, **multiple-cycle PSD** with intermediate heating steps could be optimized for energy efficiency.

The measured breakthrough volume of  $\sim 120 \text{ L}\cdot\text{g}^{-1}$  for isoprene on Carbopack B at 22 °C is high compared with literature values reported for many VOCs on other graphitized carbons (typically  $1\text{--}20 \text{ L}\cdot\text{g}^{-1}$ , depending on volatility and sorbent type), and is consistent with the intended role of Carbopack B as a strong preconcentration sorbent for very volatile organics.<sup>9, 10</sup>

An additional advantage of Carbopack-type adsorbents is their low affinity for permanent gases and water, so that, provided the gas is kept non-

condensing through the trap (e.g. with a simple cooler and modest heating of the trap above gas temperature), they selectively retain isoprene while allowing N<sub>2</sub>, O<sub>2</sub> and water vapour to pass, simplifying downstream desorption and condensation.

### Energy and Operational Trade-offs

For graphitized carbon adsorbents such as Carbopack B, and more generally for weakly to moderately bound VOCs, the main regeneration options can be compared as follows:

*Table 4.1. Considerations for Cabopack B-type adsorbents.*

Method	Temp.	Press.	Time scale	Energy Cost*	Product Conc.*	Scalability
<b>TSD (standard)</b>	200-330 °C	1 atm	10-30 min	~100-250 kJ/g isoprene	High >90%	Good for small beds; equipment cost
<b>PSD + mild heat</b>	80-100 °C	10 mbar	20-60 min	~45-60 kJ/g isoprene	Mid 50-80%	Requires vacuum pump; cont. operation harder
<b>N<sub>2</sub> stripping (25 °C)</b>	25 °C	1 atm	Hours	Low thermal, but high gas vol.	Very low <10%	Impractical massive dilution

*\*Indicative, method- and hardware-dependent.*

**Conclusion for primary capture strategy:** The cost of Carbopack B (€80/g) makes it unsuitable as a primary bulk adsorbent. Its excellent properties make it ideal for **analytical sampling and secondary polishing** (removing <10 ppm residual isoprene after primary capture). If a solid adsorbent is to be used for the pilot bioreactor, **hydrophobic silica gel** (Section 4.2, lower cost, good isoprene affinity) even though not experimentally tested by us, should be the primary adsorbent, with potential Carbopack B polishing stage downstream.

## 4.2. Hydrophobic silica gel performance

Hydrophobic silica gels (e.g. silylated grades with surface areas in the 100-300 m<sup>2</sup>·g<sup>-1</sup> range) are widely reported to provide good adsorption of non-polar VOCs at ambient temperature, with low affinity for water and regeneration by modest heating. For isoprene at 25 °C and 100-150 ppm in humid gas, such materials are therefore strong candidates for a primary solid-phase trap in place of high-cost graphitized carbons. On a per-gram basis, silica gels are typically two orders of magnitude cheaper than Carbopack B (≈€0.50-2 per gram vs. ≈€80 per gram), which is critical for any scale-up beyond analytical tube formats.

In this deliverable, hydrophobic silica gel has not yet been tested experimentally under the specific ALFAFUELS off-gas conditions. Instead, its suitability is inferred from published VOC adsorption data, its known thermal stability, and its use in industrial VOC recovery. Future work (beyond the present reporting period) will focus on quantifying, for isoprene: (i) adsorption equilibrium at 25 °C and 100-150 ppm, (ii) loading kinetics and saturation time, (iii) desorption efficiency at 30-60 °C in sealed systems without stripping gas, (iv) thermal cycling stability over multiple adsorption–desorption cycles, (v) and a direct comparison with Carbopack-type adsorbents on a per-gram and per-volume basis.

## 4.3. Aqueous partitioning and off-gas isoprene measurements

### Background and Context

Recent experimental and theoretical analysis highlight the critical importance of aqueous phase partitioning via Henry's law, which significantly affects off-gas quantification during calibration and measurement--especially for setups where isoprene is produced or injected into a water-filled bubbler and the gas phase is sampled for quantification (PID/GC).

### Henry's Law and Partitioning

Henry's law relates equilibrium between gas-phase and dissolved isoprene:

$$p_i = K_H \cdot x_i$$

where:

- $p_i$  = partial pressure of isoprene in headspace (bar)
- $K_H$  = Henry's law constant ( $\text{bar}\cdot\text{m}^3\cdot\text{mol}^{-1}$ )  
(alternative units  $\text{mol}\cdot\text{kg}^{-1}\cdot\text{bar}^{-1}$  or  $\text{mol}\cdot\text{L}^{-1}\cdot\text{bar}^{-1}$ )
- $x_i$  = mole fraction of isoprene in water

### Henry's Law Constants for Isoprene

Henry's constant,  $K_H$ , is in the range  $0.013\text{-}0.028 \text{ mol}\cdot\text{kg}^{-1}\cdot\text{bar}^{-1}$  and is valid at  $25^\circ\text{C}$  (Typical range; slight variation by source)<sup>1, 12</sup>

Source: Sander<sup>1</sup> and using standard chemical-engineering relations and notation (e.g. Perry's Chemical Engineers' Handbook)<sup>12</sup>.

### Gas-Phase ppm to Partial Pressure Conversion

At total pressure  $P_{\text{tot}} = 1 \text{ atm}$  ( $1.013 \text{ bar} \approx 763 \text{ mmHg}$ ):

$$p_i = \frac{\text{ppm}}{10^6} \times P_{\text{tot}}$$

### Examples:

- $100 \text{ ppm} \rightarrow p_i = 1.0 \times 10^{-4} \text{ bar} = 0.1 \text{ mbar}$
- $150 \text{ ppm} \rightarrow p_i = 1.5 \times 10^{-4} \text{ bar} = 0.15 \text{ mbar}$
- $300 \text{ ppm} \rightarrow p_i = 3.0 \times 10^{-4} \text{ bar} = 0.3 \text{ mbar}$

### Dissolved Isoprene in Water at Different ppm Levels

Using  $K_H = 0.013 \text{ mol}\cdot\text{L}^{-1}\cdot\text{bar}^{-1}$  at  $25^\circ\text{C}$ :

*Table 4.1. Dissolved isoprene concentration in water at various gas-phase ppm levels*

Gas-Phase ppm	Partial Pressure (bar)	Dissolved $c_{\text{aq}}$ ( $\text{mol}\cdot\text{L}^{-1}$ )	Dissolved $c_{\text{aq}}$ ( $\text{mg}\cdot\text{L}^{-1}$ )
100	$1.0 \times 10^{-4}$	$1.3 \times 10^{-6}$	0.089
150	$1.5 \times 10^{-4}$	$1.95 \times 10^{-6}$	0.133
300	$3.0 \times 10^{-4}$	$3.9 \times 10^{-6}$	0.266
500	$5.0 \times 10^{-4}$	$6.5 \times 10^{-6}$	0.443

**Key conclusion:** At ppm-level gas-phase isoprene concentrations (typical for bioreactor off-gas), the equilibrium dissolved concentration in water is

**sub-mg·L<sup>-1</sup>** (order 0.1-0.5 mg·L<sup>-1</sup>). Water does **not** act as a strong buffer or sink at these partial pressures; most isoprene stays in the gas phase during normal operation.

### Implications for laboratory test systems

1. **Gas-phase concentrations are not strongly suppressed by water contact.** At the low partial pressures corresponding to 100-300 ppm, water can hold only fractional mg/L of isoprene at equilibrium; therefore isoprene in a 1 L reactor with 6 mg/h production rate will mostly be in the gas phase, not lost to water.
2. **Aqueous partitioning is negligible during capture operations.** The capture modules (TSC, LAC, adsorption) operate on humidified gas at ppm levels; Henry's law predicts only 0.1-0.5 mg/L dissolved in any associated condensate, so losses to water are minimal compared to the main gas-phase stream.
3. **Calibration and measurement implications remain.** In contrast to high-concentration systems (e.g., injecting pure liquid isoprene into a 1 L water bath), low-ppm gas streams reach equilibrium quickly without significant signal loss.

This analysis explains why the present capture and calibration experiments are designed around dry or humid gas streams and organic trapping solvents, and why water cannot be considered a significant isoprene sink.

## 4.4. Determination of partitioning coefficients

### 4.4.1. Online gas analysis

Real-time isoprene quantification employed a IonScience Tiger XLT (ppb) Photoionization Detector (PID) configured for ppb-to-ppm measurements. The PID uses an ultraviolet lamp (10.6 eV photon energy) to ionize isoprene and other volatile organic compounds. The detector response is instantaneous (~1 s) and proportional to analyte concentration.

### 4.4.2. System description and methodology

An experimental system has been developed to characterize the equilibrium and dynamic release of isoprene from loaded solvents during regeneration. In this configuration, a known amount of isoprene is added

to a known volume of candidate trapping solvent in a closed vessel and equilibrated at a set temperature in the range 0-45 °C. The vessel headspace is connected to a Photoionization Detector (PID) with a pump rate of 220 mL·min<sup>-1</sup> and to a breather line that admits make-up air, such that the air enters at the bottom and bubbles through the solution, maintaining near-ambient pressure in the vessel (Figure 4.4). The PID reading of the isoprene concentration  $c_i$  [ppm] is recorded continuously as the gas flow strips off isoprene from the solvent. To avoid temperature change in the sample the breather line was submerged in the same cooling bath as the sample vessel. Initially a 100 mL Schott flask with 10 mL of sample and gas sparger was used, but it was later replaced by 30 mL test tubes with septum and 2 cm of glass beads (Figure 4.5). The test tubes improved the gas-liquid contact and allowed for addition of isoprene and mixing, ahead of the desorption initiation.



*Figure 4.4. PID analyser sampling a test tube, connected with a breather line (at ambient temperature).*



Figure 4.5. Test tubes with glass beads used for experiments.

### 4.4.3. Physical interpretation and thermodynamic basis

A simple desorption model was developed to extract partitioning (Henry) coefficients  $K$  for isoprene in each solvent. Starting from a molar balance on isoprene in a flow-through desorption cell, the model assumes that the liquid phase is well mixed, that gas and liquid remain in near-instantaneous equilibrium, and that isoprene is present at low mole fraction compared with the solvent. Under these conditions, the equilibrium relation between liquid- and gas-phase compositions can be written in terms of a partition coefficient  $K$ ,

$$K = \frac{p_i \text{ (bar)}}{c_{\text{liquid}} \text{ (mol/L)}}$$

where  $p_i$  is the partial pressure of isoprene in the gas phase and  $c_{\text{liquid}}$  is the concentration of dissolved isoprene in the solvent. The mass balance (as derived in Appendix D, section 9.49.4) describes a first-order decay in the off-gas concentration. This leads to a linear relationship between the natural logarithm of the measured gas-phase concentration and time, so that  $K$  can be obtained directly from the slope of  $\ln(c_i)$  versus time using known values of gas flow rate, temperature and solvent inventory. At the low loadings relevant here, the resulting  $K$  values are equivalent to Henry's constants for isoprene in the different trapping media and provide a compact, thermodynamically grounded way to compare solvent performance.

By repeating the experiment at different temperatures in the range 0-45 °C the temperature dependence of  $K$  could also be established. These results make it possible to model the absorption of isoprene from a bioreactor bleed gas, as well as the desorption step at suitable pressures and temperatures, providing essential data for a design.

#### 4.4.4. Experimental results

The four candidate solvents considered were 1-octanol, H350 (thermal fluid based on dibenzyl toluyl-derivative), HL60 (trade name for PDMS silicon oil), and isoprene dimer. The dimer available was produced by photocatalysis in previous ALFAFUELS trials, but even after vacuum treatment and prolonged sparging the PID background was too high to be used in experiments. Unfortunately, results could also not be obtained for PDMS using the PID instrument. Even though the silicone oil has a very low vapour pressure, it turned out to be incompatible with the PID instrument most likely due to aerosolization and fouling of the detector, resulting in a rapid degradation of sensitivity that could only be regained by thorough cleaning of the instrument and polishing of the ionization lamp.

PID logs show decay curves that for a large portion are reasonably well described by a single-stage, first-order desorption model, suitable for analysis with the linearized  $\ln(c)$ -vs-time method described above. Typically, the signal was transient for a while in the beginning of the experiments, before steadily decaying towards the background level. The PID is very sensitive and even these high-boiling solvents produced measurable backgrounds. As can be seen in Figure 4.6 and Figure 4.7, the curves plateau at higher concentrations at higher temperatures.

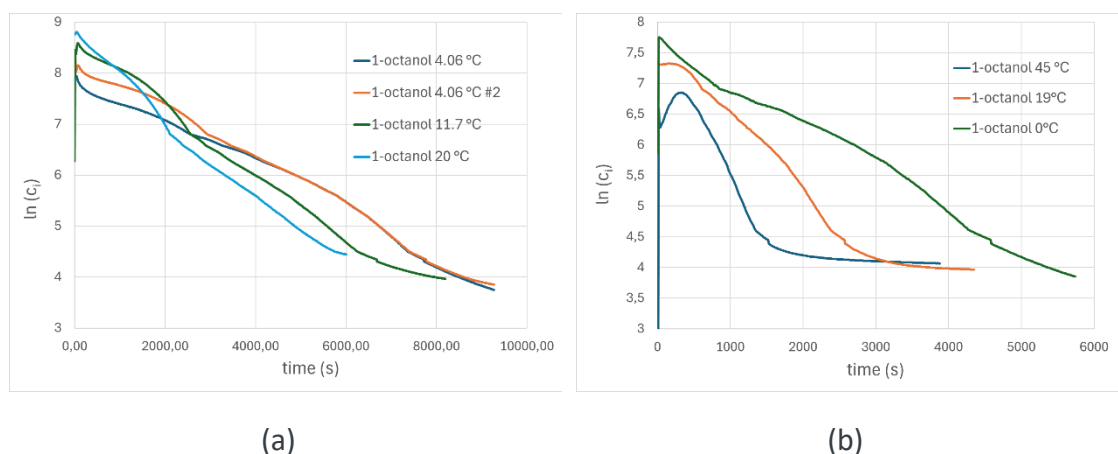


Figure 4.6. Result from a series of desorption experiments from 1-octanol, (a) in the early setup using a 100 mL flask, (b) in 30 mL test tubes with glass beads.

1-octanol behaved well over the studied temperature range and produced the most consistent results. Figure 4.6 shows two series of experiments using the two described setups. A steeper slope (in the linear region) means a lower K value, e.g. 1-octanol at 45 °C (blue line in Figure 4.6 b) dissolves less isoprene than at lower temperatures. As can be seen in Figure 4.8. Temperature dependence of partitioning coefficients K. the improved bubbler yielded slightly higher K values, but the reason is not clear. The temperature dependences were however almost identical with a slope of 2440 K.

H350 turned viscous at low temperatures and when isoprene was injected at 6 °C there were difficulties mixing it with the solvent in the early setup using 100 mL flasks. This is most likely the reason for the initially high concentration ( $c_i$ ) of isoprene in the gas phase, as seen in Figure 4.7. The resulting K values presented in Figure 4.8 tend to be higher than for 1-octanol, but since the points at different temperatures do not fall well on a line, this apparent improvement is uncertain.

It should be noted that the determination of K does not rely on a correctly calibrated PID, as long as the measured value is proportional to the gas phase concentration  $c_i$  of isoprene. Since the natural logarithm of the concentration vs time is evaluated, a PID response factor error will only produce a vertical shift of the plot but result in the same slope. When calculating a K value from such a slope, the volumetric gas flow and the amount of absorbing solvent (mol, kg, or liter depending on the unit used)

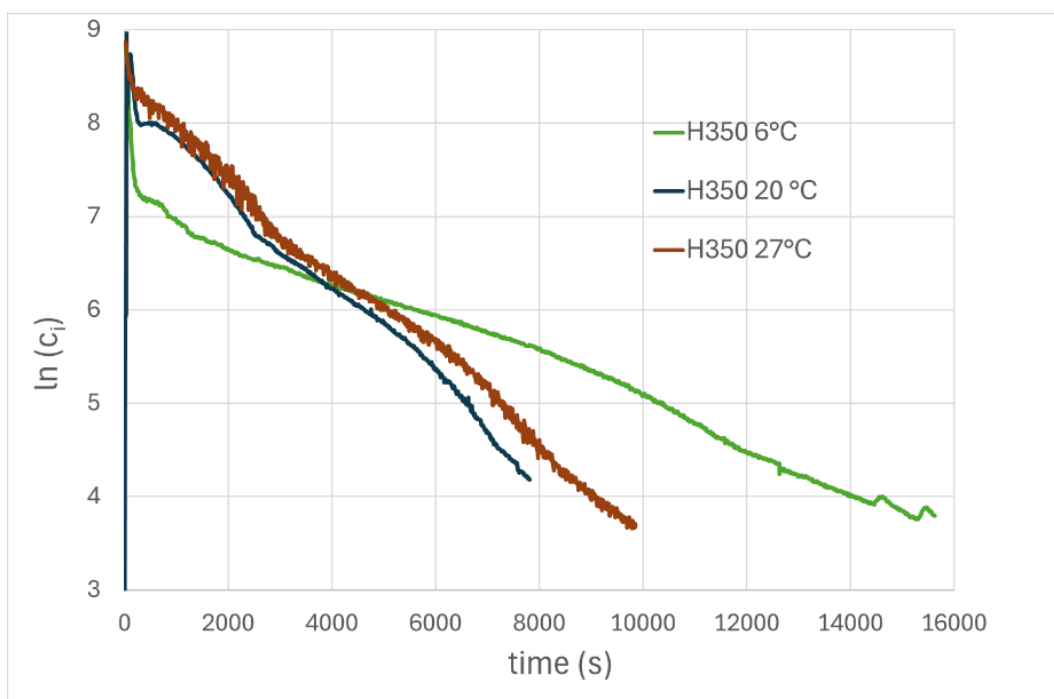


Figure 4.7. Results from a series of desorption experiments from H350

are critical. In the determinations above the actual PID flow was not measured, but rather the datasheet value was used. This may very well explain the difference between the two 1-octanol series seen in Figure 4.8.

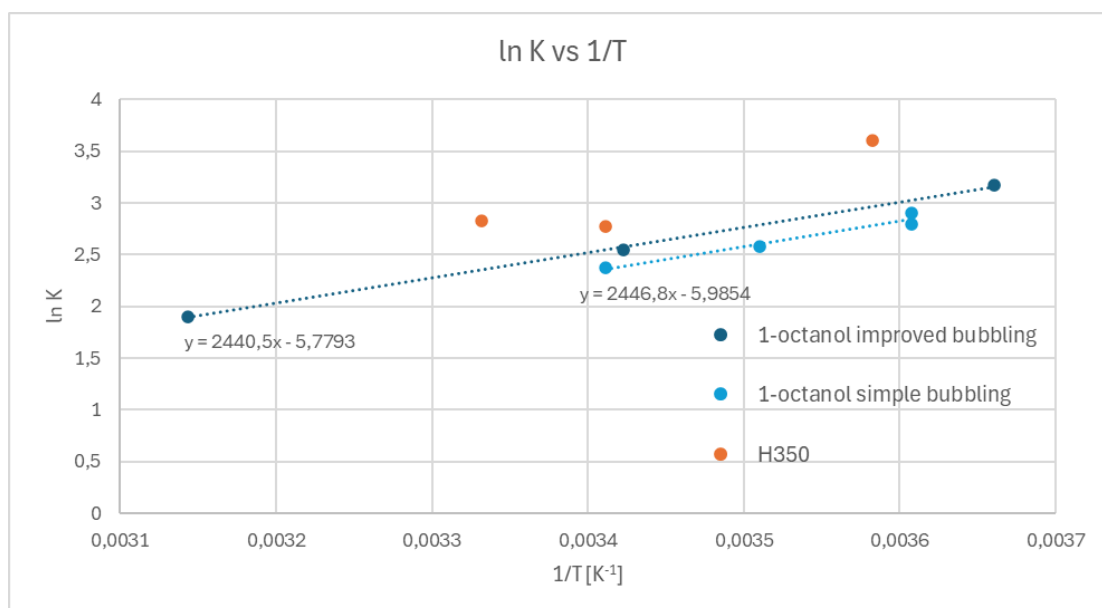


Figure 4.8. Temperature dependence of partitioning coefficients  $K$ .

## 4.5. Liquid absorption capture test

### 4.5.1. Simulation of LAC using 1-octanol

Using the partitioning constant  $K_H$  and its temperature dependence it is possible to simulate absorption and desorption systems. Determined partitioning constant were therefore inserted in the mass balance equations for the test rig described in the following section, in part to visualize the expected outcome, but also to compare obtained results from the desorption and absorption studies.

Figure 4.9 shows (a) the ideal outflow concentrations of isoprene after one stage and two stage absorption in 1-octanol, as well as (b) the expected concentration of isoprene caught in a cold trap after the absorption stages. Conditions were chosen to be 50 NmL/min gas flow with 373 ppm isoprene, 10 mL 1-octanol at 0 °C in the absorption stages, and 20 mL of liquid in the final cold trap.

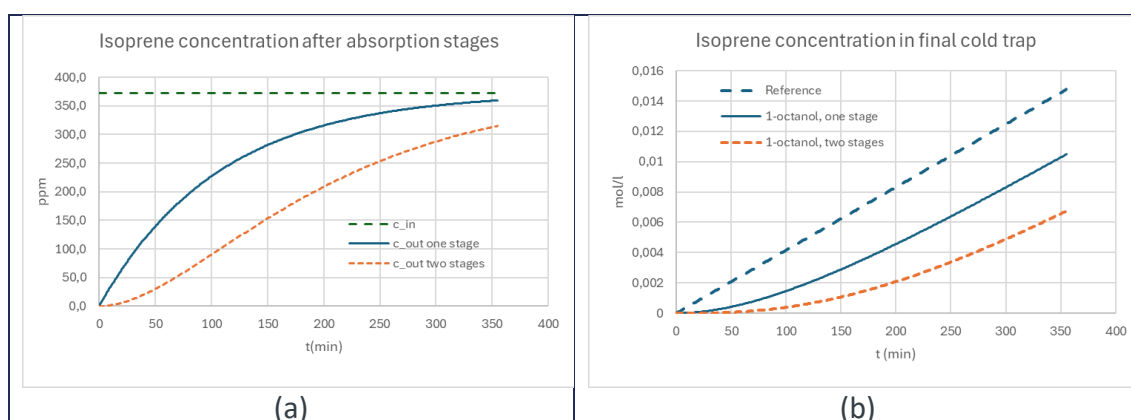


Figure 4.9. Simulated isoprene absorption using one and two absorption stages in 1-octanol. The reference line in figure (a) corresponds to 373 ppm isoprene, and the reference in figure (b) corresponds to no absorption and that all isoprene ends up in the final cold trap.

A dramatic improvement in trapping efficiency when using multi-stage systems is evident from the figures. As an example, with a single step a 50-ppm slip in the outflow is reached after about 15 min. Doubling the absorption liquid volume in the single stage would double that time to 30 min, but if the same volume is instead divided over two consecutive stages, the on-stream time before reaching 50 ppm after the traps will increase to more than an hour. Although this assumes a system of ideal behaviour, simulations like this are very useful tools when designing separation system.

Another way to represent this in terms of recovery efficiency is a single stage system of 20 mL decreases from 100% efficiency at  $t=0$  min to 87%

after one hour. A two-stage system with two 10 mL flasks will reach 87% efficiency after more than two hours. More stages can of course be added in this simulation, extending this to a counter-current LAC-column with any number of bottoms. An isoprene stripping section can be analysed in the same manner.

Since only low concentration can ever be reached in a solvent (given the derived Henry's), a certain volume of solvent can only be used as an absorption liquid for a limited period before trapping efficiency has dropped below the design threshold. Therefore, it is difficult to express the results in terms of recovery efficiency without specifying the time-on-stream. The LAC-liquid needs to be regenerated to be recycled and to release isoprene, which quickly becomes costly at large volumes regardless of good energy efficiency. The best way to keep the solvent volume low while maintaining a good recovery efficiency is to use a continuous multi-stage system, which translates into a counter-current LAC-column (discussed more in section 6.2).

#### 4.5.2. Test rig for LAC

To quantify solvent-based trapping efficiency for isoprene at ppm-level concentrations, a dedicated flow-through test rig has been constructed. A flow-controlled N<sub>2</sub>/isoprene gas stream (optionally with CO<sub>2</sub> and humidity to mimic bioreactor off-gas) is passed first through an empty LAC trap kept at ambient or slightly elevated temperature, and then into a -40 °C heptane final trap used as a quantitative reference. In this baseline configuration, the LAC trap contains no solvent, so essentially all isoprene is captured in the final heptane trap and quantified by GC, establishing the reference mass flow of isoprene.

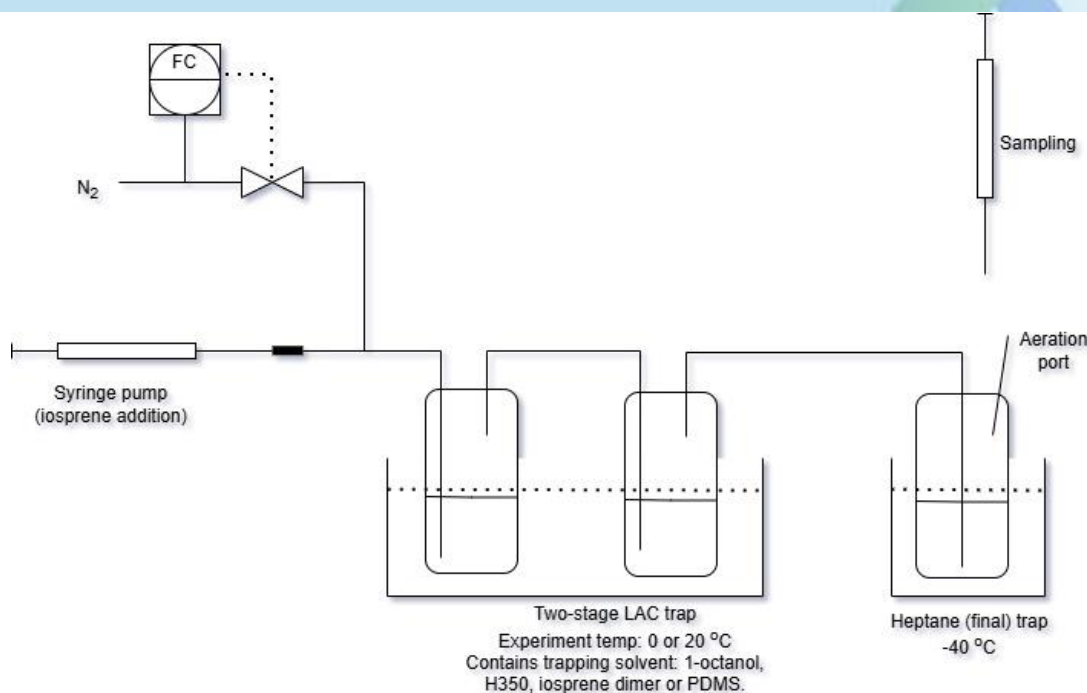


Figure 4.10. Schematic LAC rig with two LAC-stages.

Figure 4.10 shows a schematic representation of the LAC test rig, photos in Figure 4.11. Initially, a single stage LAC was used.

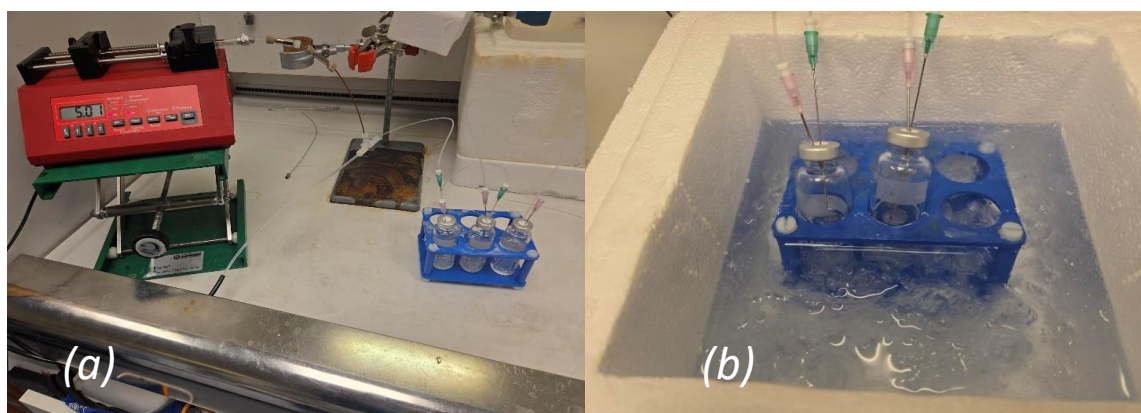


Figure 4.11. Photos of the LAC rig, showing syringe pump and partial trap at room temperature (a) and partial trap at 0 °C (b).

In experimental runs, the partial trap has been filled with a candidate trapping solvent (e.g. PDMS, isoprene dimer product, Thermal H350, 1-octanol) and operated at a defined temperature, while the downstream heptane trap and GC analysis remain unchanged. The reduction in isoprene reaching the final trap, relative to the baseline case, directly yields the trapping efficiency of the solvent system under realistic low-concentration conditions. This configuration avoids direct GC injection of high-boiling

trapping solvents and enables systematic screening of solvent type and temperature while keeping the analytical protocol identical.

### 4.5.3. Results from LAC

To quantify solvent-based trapping efficiency for isoprene at ppm-level concentrations, a dedicated flow-through LAC test rig was constructed. A flow-controlled N<sub>2</sub>/isoprene gas stream is passed first through a LAC trap operated at a defined temperature and then into a -40 °C heptane final trap used as a quantitative reference. In the baseline configuration, the partial trap contains no solvent, so essentially all isoprene is captured in the final heptane trap and quantified by GC-FID, establishing the reference mass flow and GC response.

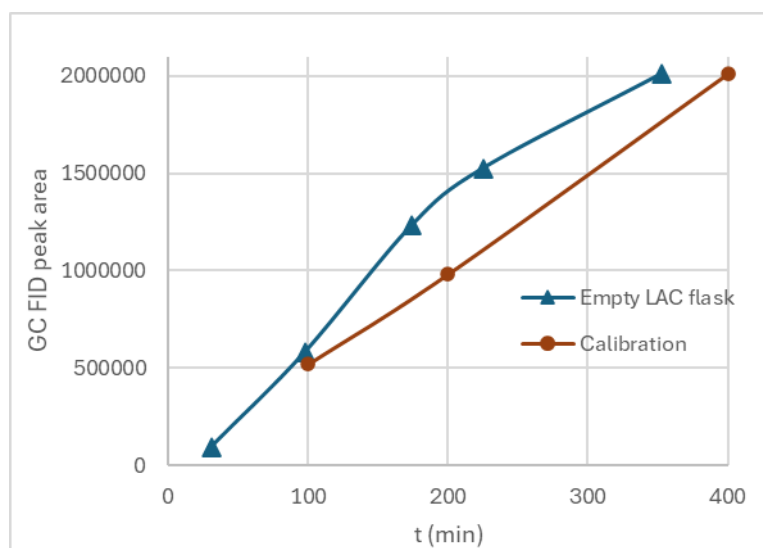


Figure 4.12. Comparison of two reference experiments

To investigate data integrity in using several flasks in series, sampling inconsistencies etc, an ideal baseline was measured by directly trapping isoprene from the syringe pump in heptane, simulating the baseline configuration in a reduced system. The results that can be seen in Figure 4.12 indicate a deviation between the two reference cases of ca 10-20%.

In experimental runs, the partial trap was filled with a candidate trapping solvent (e.g. 1-octanol, Thermal H350 or PDMS) and operated either as a single conical flask or as a two-stage vial system with glass beads to enhance sparging and interfacial area. The reduction in isoprene signal reaching the final trap, relative to the empty LAC baseline, provides a direct measure of trapping performance under realistic low-concentration conditions, while avoiding direct GC injection of high-boiling solvents.

**Trapping efficiency:**  $\eta_c = 1 - \frac{C_{out}}{C_{in}}$

In practice,  $C_{in}$  is taken from the empty LAC baseline and  $C_{out}$  from the solvent run at comparable operating conditions.

Figure X shows GC-FID peak area versus time for four cases: (i) empty LAC trap, (ii) 1-octanol at 0 °C, (iii) H350 at 20 °C, and (iv) a two-stage 0 °C HL60 (trade name for PDMS) configuration with glass-bead-filled vials to promote gas–liquid contact. The empty LAC curve rises rapidly and nearly linearly, confirming that essentially all dosed isoprene reaches the final trap. In contrast, the single-stage solvent curves (1-octanol and H350) grow much more slowly and to substantially lower total area, while the two-stage curve remains close to the detection limit throughout the experiment (inset), indicating very strong capture.

Because the time series are limited and there are no experimental replicates, trapping performance was first assessed in a deliberately low-level way. At selected time points where all configurations have data, the instantaneous trapping efficiency was estimated as  $\eta_c(t) = 1 - A_{solv}(t)/A_{ref}(t)$ , with  $A_{ref}(t)$  and  $A_{solv}(t)$  the GC-FID peak areas for the baseline and solvent cases at time  $t$ . These pointwise comparisons consistently show substantial attenuation for the single-stage solvents and very low residual signals for the two-stage trap, even when data scatter is taken into account.

To obtain a more robust, though still approximate, measure of overall recovery, the cumulative peak areas of non-trapped isoprene were also fitted with simple linear regressions over the linear portions of each curve. The ratio of fitted slopes,  $A'_{solv}/A'_{ref}$ , provides an alternative estimate of average slip through the trap, and hence of  $\eta_c \approx 1 - A'_{solv}/A'_{ref}$ , that is less sensitive to point-to-point noise. Both the single-point and linear-fit approaches agree qualitatively: the specific choice between 1-octanol and H350, and the modest temperature difference tested, have a smaller influence than the capture geometry, whereas the two-stage 0 °C configuration achieves near-complete trapping under these conditions.

Given the absence of replicates and the limited time range, these LAC results should be regarded as preliminary and mainly indicative of trends. Even so, they support the design conclusion that improving gas–liquid contact (staging, packing, sparging) is a more powerful lever for isoprene

recovery than fine-tuning solvent chemistry within the tested group, and they provide first quantitative estimates of  $\eta_c$  that can be used in the preliminary sizing of pilot-scale capture modules.

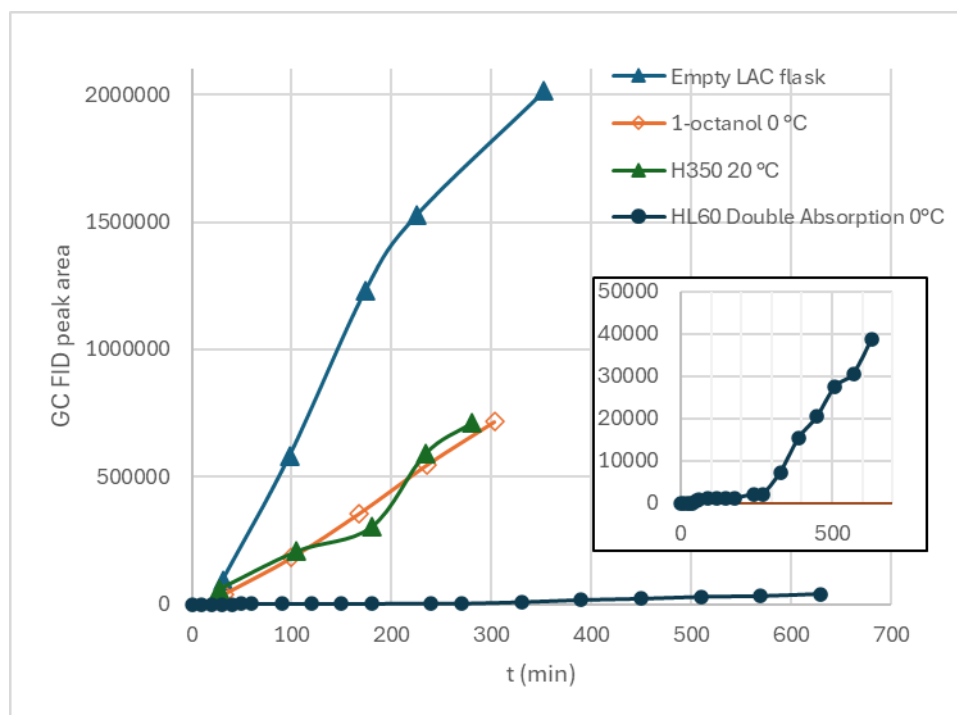


Figure 4.13. Determination of LAC trapping efficiency. Inlay shows a magnification of the HL60 double absorption experiment.

The linear regression gave estimated recovery rates for 1-octanol (at 0 °C) and H350 (at room temperature) as 58% and 57%, respectively. It should be noted that H350 is at a much higher temperature and as seen from the partitioning coefficients (e.g. Figure 4.8), temperature have a considerable effect on the trapping efficiency which indicates the effectiveness of H350 as a trapping solvent. Gas sparging is also less efficient at higher viscosity without directed sparger design, again endorsing the efficiency of H350. However, as previously mentioned, H350 becomes very viscous already at 0 °C, so it is already at it's lower temperature limit at room temperature.

In section 4.5.1 the partitioning coefficients derived from the desorption tests for 1-octanol has been used to simulate isoprene capture for one or two stages. The conclusion is that

## 4.6. Direct condensation – preliminary considerations

At bioreactor off-gas conditions (100-150 ppm, 25 °C ambient), isoprene is far above its dew point and remains fully gaseous. Hence condensation requires cooling to –45 to –55 °C and any measurable amounts are detected at moderate cooling (–5 to –10 °C) this can be explained by that kinetic nucleation can initiate droplet formation but in general, equilibrium condensation is negligible. For more details, see Appendix C.

# 5. Gas-flow design and isoprene stripping

## 5.1. Design framework: linking productivity, gas flow, and off-gas ppm

The relationship between isoprene productivity, gas flow, and resulting off-gas concentration is:

$$C_{\text{ppm}} = \frac{n_{\text{iso}} \times 10^6}{n_{\text{gas}}}$$

where:

- $n_{\text{iso}}$  = molar production rate ( $\text{mol}\cdot\text{h}^{-1}$ )
- $n_{\text{gas}}$  = molar gas flow ( $\text{mol}\cdot\text{h}^{-1}$ )

At 25 °C and 1 atm (molar volume =  $24.45 \text{ L}\cdot\text{mol}^{-1}$ ):

$$C_{\text{ppm}} = \frac{r_{\text{mass}}}{M_{\text{iso}} \times Q_{\text{gas}}/24.45} \times 10^6/3600$$

For a baseline productivity of  $r = 6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  per litre of culture, the required gas flow to achieve a target ppm is:

$$Q_{\text{L}/\text{min}} = \frac{r_{\text{mg/L/h}} \times 24.45}{M_{\text{iso}} \times C_{\text{ppm}} \times 10^{-6} \times 60}$$

## 5.2. Design table: gas flow for target isoprene concentrations

The table below shows the required gas flow (in  $\text{L}\cdot\text{min}^{-1}$  per litre of culture) to achieve steady-state isoprene concentrations of 100, 150, 300, and 500 ppm at  $6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  productivity:

*Table 5.1. Gas flow requirements for target isoprene concentrations at  $6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  productivity*

Target ppm	Q ( $\text{L}\cdot\text{min}^{-1}$ per L culture)	Q ( $\text{mL}\cdot\text{min}^{-1}$ per L culture)	vvm
100	0.359	359	0.359
150	0.239	239	0.239
300	0.120	120	0.120
500	0.072	72	0.072
2000	0.018	18	0.018
7000	0.005	5	0.005

**Example:** To maintain ca 150 ppm isoprene in the off-gas at  $6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  productivity, a gas flow of  $0.24 \text{ L}\cdot\text{min}^{-1}$  per litre of culture (0.24 vvm) is required.

Gas flows in the 0.05-0.3 vvm range are already established for  $\text{CO}_2$  supply and culture mixing in photobioreactors (see Section 3.1).<sup>14</sup>

## 5.3. Bleed stream and make-up gas strategy

In practice, the culture loop is sparged at the "biologically optimal" flow (eg 0.25 vvm) to ensure adequate  $\text{CO}_2$  supply, culture mixing, and **oxygen stripping**.

**Oxygen production and removal:** In oxygenic photosynthesis, approximately **5 mol of  $\text{O}_2$  is evolved per mol of isoprene produced** (from  $\text{CO}_2$ -fixation stoichiometry; this is an upper bound, as some  $\text{O}_2$  is consumed by respiration). At  $6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  isoprene ( $0.088 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ ), this corresponds to roughly  $0.44 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  of  $\text{O}_2$  evolution. If  $\text{O}_2$  accumulates unchecked, it can become toxic to the culture. However, as explained in section 3.1, these concerns seem to be of low relevance.

### Recommended operational mode:

1. The culture loop circulates at the full biological sparge rate (e.g. 0.25 vvm) to meet  $\text{CO}_2$  and mixing requirements.

2. A **side-stream bleed** ( $Q_{\text{bleed}}$ ) is continuously removed from the recirculated gas, passed through capture modules (TSC/silica gel/PDMS), and vented.
3. **Make-up gas** ( $\text{N}_2 + 3\text{-}4\% \text{CO}_2$ ) is added to:
  - Restore total circulation flow and  $\text{CO}_2$  supply.
  - Dilute residual  $\text{O}_2$  in the recycle loop, mitigating oxidative stress.
4. The bleed flow  $Q_{\text{bleed}}$  is sized (using the design table above) to give a target isoprene ppm in the bleed stream, optimizing capture efficiency while avoiding over-stripping.

**Example:** If the full loop operates at 0.25 vvm and a target bleed ppm is 500 ppm, then  $Q_{\text{bleed}} \approx 0.072$  vvm (from Table above), with the remaining  $\sim 0.178$  vvm recirculated back to the reactor as make-up. In practice, some recirculation (not pure bleed) may be preferable to maintain stable loop dynamics.

This approach decouples biological gas requirements from isoprene extraction, allowing flexible tuning of capture intensity without compromising culture health.

## 5.4. Temperature dependence of Henry's constant

At higher temperatures, Henry's constant  $H$  (or equivalently,  $k_H$ ) decreases, shifting the aqueous-gas equilibrium toward the gas phase. This can be exploited:

Raising reactor temperature to 30-40 °C (within growth tolerance) increases gas-phase isoprene concentration and reduces aqueous buffering.

## 5.5. Considerations for photobioreactor geometry, gas flow scaling, and isoprene stripping

WP6 will focus on detailed photobioreactor design and model-based optimisation, informed by the gas-flow, stripping and capture considerations developed in this deliverable together with other design inputs from the consortium. Key aspects include: (i) reactor geometry and

light-path design to balance surface-to-volume ratio, footprint and ease of scaling; (ii) gas-flow configuration (sparging vs. headspace sweep, bleed/make-up strategy) to reach target off-gas isoprene levels at sub-0.3 vvm aeration rates; and (iii) hydrodynamics and mixing to avoid dead zones and ensure uniform light exposure, CO<sub>2</sub> supply and efficient stripping of volatile products. The design of the integrated system - the PBR and the recovery system - should also account for biological performance constraints (growth, oxygen tolerance) and practical control concepts (on-line gas analysis, feedback on gas flow and light) so that the final PBR design remains compatible with the capture and regeneration modules outlined in WP5 and with subsequent upscaling in WP7.<sup>15, 16, 17</sup>

## 6. Conclusion for capture strategy: integration and comparison

The process design developed in this work combines two independent but compatible capture concepts, which are supported by literature and preliminary engineering analysis as well as some experimental data, but remain to be validated under full ALFAFUELS conditions.

### 6.1. Capture strategies

#### **Path A: Liquid-Phase Absorbent (e.g. PDMS)**

- Conceptual advantages: Higher loading per unit volume than solids, tuneable contactor design, and compatibility with standard gas–liquid absorption equipment.
- Intended integration: Absorber column on the bioreactor gas outlet, for multi-stage absorption with PDMS circulated between the absorber and a heated regeneration vessel.
- Expected desorption mode: Heating the loaded PDMS (e.g. 30–40 °C) with ideally no inert gas to generate an isoprene-enriched headspace suitable for condensation or direct use.
- Open points: Long-term solvent stability, impurity build-up and practical regeneration rates require experimental verification.

#### **Path B: Solid-Phase Adsorbent (Hydrophobic Silica Gel)**

- Conceptual advantages: No moving parts, minimal solvent handling, straightforward recharging.

- Intended integration: Fixed-bed adsorber placed on the bioreactor gas outlet or bleed stream.
- Expected desorption mode: Gentle heating in the ~30–60 °C range in a sealed or semi-closed vessel to release isoprene-rich vapour, avoiding large stripping-gas flows.
- Open points: Actual working capacity, cycle stability and cost per cycle for isoprene service remain to be established experimentally.

#### **Comparison with patent approaches:**

- WO2011075534 A2 employs long-chain hydrocarbon solvents in large, industrial absorption–stripping loops with heated reboilers and condensers.
- The proposed PDMS and optional silica-gel scheme targets pilot scale (10–100 L reactors), where reduced complexity and lower sorbent/solvent cost are prioritized over maximal thermodynamic efficiency.
- Operation at lower regeneration temperatures and with minimal stripping gas is intended to reduce both energy demand and product dilution relative to the 60–80 °C + inert-gas stripping regimes described in the patents.

#### **Potential combined operation (conceptual):**

- TSC + silica gel: A cooling step removes water to prolong the working life of the downstream silica; a downstream silica-gel bed is then used to trap isoprene.
- TSC + PDMS: Cooling removes water in the gas; PDMS absorption captures most of the residual isoprene in a multi-pass or recycled configuration.
- Silica gel + PDMS in series: A solid bed upstream of a PDMS absorber can distribute the capture load and maximize overall recovery

These arrangements have not yet been tested experimentally in ALFAFUELS and with the design suggested in 6.2.

## **6.2. Condensation and absorption modules**

A process diagram for a continuous liquid adsorption capture system is exemplified in Figure 6.1., including a pressure-swing desorption system for final isoprene recovery. The key components of the system will be

described and commented below. Figure 6.1. Overview of a continuous multistage LAC system for isoprene separation

**TSC unit:** A water condensation trap at 0 °C to decrease the risk of condensation of the water-saturated and warm bleed gas from the PBR in the LAC column.

**LAC column (LAC):** A low-volume bubble cap column (ID 10-25 mm) with counter-current PDMS flow. PDMS was used as a liquid phase absorbent, motivated by:

- Literature data on PDMS sorption of hydrophobic VOCs<sup>5, 6</sup>
- Low vapor pressure (~0.1 Pa at 25 °C), minimal solvent evaporation loss
- Moderate isoprene solubility (Henry's constant similar to light alkanes), but as high as can be expected from any solvent in the ALFAFUELS system.
- Easy thermal regeneration at 30-40 °C without stripping gas
- Readily available at moderate bulk cost

**PSD unit:** The pressure-swing desorption unit comprises a membrane pump that transports headspace gas from the column, thereby lowering the column pressure and simultaneously compressing the gas into a cooled condensation unit. Liquified isoprene is collected after condensation and since it is pressurized it can in principle be fed directly into the photochemical reactor (WP7). Isoprene saturated solvent from the LAC column bottom can be aspirated into the PSD unit since it operates under reduced pressure. To further aid the desorption the column is mildly heated.

#### **Module design:**

- **Absorption column:** Bubble cap geometry, 10-25 mm ID
- **PDMS loading and flow:** To be measured, kept as low as possible
- **Gas-liquid contacting:** Counter-current gas-liquid flow
- **Desorption protocol:** Heating to 30-40 °C in PSD-column, similar to LAC-column
- **Isoprene concentration measurement** at critical points

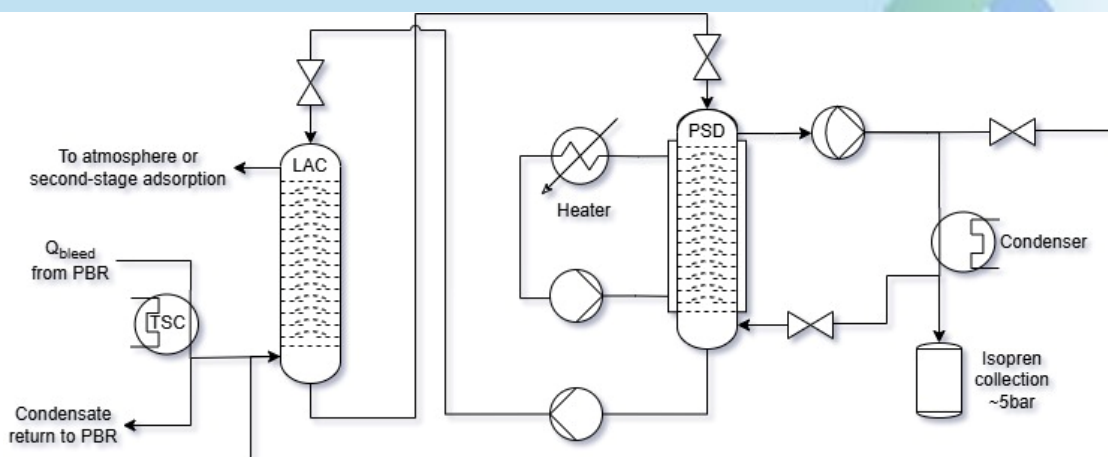


Figure 6.1. Overview of a continuous multistage LAC system for isoprene separation

## 7. Conclusions

- **Hydrophobic silica gel and PDMS absorption** provide scalable, cost-effective capture routes complementary to existing TSC and LAC methods. Together with patent literature (WO2011075534 A2, EP2980221 A1), these approaches span the practical solution space for ppm-level isoprene recovery from bioreactors.
- **Low-temperature desorption (30-40 °C, no external stripping gas)** offers significant energy and operational advantages over conventional TSD and PSD, particularly for small-to-medium scale applications.
- **PSD and TSD on Carbopack A** elucidate lower energy requirements for desorption under realistic 140 ppm feed, but is believed to be too costly for large-scale implication.
- **PID monitoring** provides real-time, direct isoprene quantification without cross-talk from carrier gas or CO<sub>2</sub>, with GC-FID verification confirming identity and accuracy. This represents a significant improvement over ratio-based mass spectrometry.
- **Combined methods** (TSC + silica gel, TSC +PDMS, or silica gel + PDMS in series) form a robust, albeit theoretical, basis for pilot-scale isoprene recovery and process intensification.
- **Aqueous partitioning via Henry's law** is essential for understanding off-gas measurements. At ppm-level isoprene concentrations, dissolved aqueous concentration is sub-mg·L<sup>-1</sup>; water does not

strongly buffer the gas phase, but Henry's law must be explicitly considered in calibration protocols.

- **Gas-flow design table** (Section 5.2) provides a practical tool for engineering gas bleed streams and make-up gas in full-scale reactors to achieve target isoprene ppm while managing O<sub>2</sub> evolution and minimizing energy cost.
- **Photobioreactor geometry and modular design** allow optimization of gas flow below linear scale-up assumptions, with energy efficiency and stripping performance to be validated in pilot and full-scale trials (D6.6, D7.1).
- **Partitioning constants** in solvents with high affinity towards isoprene is crucial for the design of LAC systems. Experimental protocols for determining partitioning constants in the candidate solvents have been established and can be used to investigate other solvent systems. The determined constants can be used to simulate different operational conditions of the separation system.
- **Experimental validation** has provided qualitative data from PDMS absorption experiments, supported by proposed P&ID diagrams (Figure 6.1). These will form the technical foundation for pilot-scale design and deployment (WP6, WP7) and technology transfer to ALFAFUELS partners.

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## 9. Appendices

### 9.1. Appendix A: Conversion between productivity, molar flow, and gas concentration

#### A.1 Formula derivation

Given:

- Productivity:  $r$  (mg·L<sup>-1</sup>·h<sup>-1</sup>)
- Gas flow:  $Q_{\text{gas}}$  (L·min<sup>-1</sup>)
- Reactor volume:  $V$  (L)

**Step 1:** Molar production rate in reactor:

$$n_{\text{prod}} = \frac{r \cdot V}{M_{\text{iso}} \times 3600 \text{ s/h}}$$

where  $M_{\text{iso}} = 68.12 \text{ g/mol}$ .

**Step 2:** Mole fraction in gas:

$$y_{\text{iso}} = \frac{n_{\text{prod}}}{n_{\text{gas}}} = \frac{n_{\text{prod}} \times 24.45}{Q_{\text{gas}} \times 60 \text{ min/h}}$$

at 25 °C and 1 atm; 24.45 L/mol is the molar volume.

**Step 3:** ppm(v/v):

$$C_{\text{iso, ppm}} = 10^6 \times y_{\text{iso}}$$

## A.2 Simplified rule at 25 °C, 1 atm

For a gas flow of  $0.25 \text{ L}\cdot\text{min}^{-1}$  per litre of culture:

$$C_{\text{iso, ppm}} \approx 24 \times r_{\text{mg/L/h}} \approx 24 \times 6 \approx 144 \text{ ppm}$$

## A.3 Example calculation

*Table 9.1. Example calculations for gas-phase isoprene concentration scaling*

Reactor Volume	Productivity	Gas Flow	Expected C_iso
1 L	$6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	$0.25 \text{ L}\cdot\text{min}^{-1}$	144 ppm
12 L	$6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	$3.0 \text{ L}\cdot\text{min}^{-1}$	144 ppm
100 L	$6 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	$25 \text{ L}\cdot\text{min}^{-1}$	144 ppm

**Note:** Assumes ideal gas, steady-state, and neglects small humidity effects.

## 9.2. Appendix B: detailed aqueous partitioning analysis and Henry's law calculations

### B.1 Henry's Law constants for isoprene

Thermodynamic notation and concepts follow standard treatments of molecular phase equilibria e.g. NIST Chemistry WebBook<sup>7</sup>, Prausnitz et al. (Molecular Thermodynamics of Fluid-Phase Equilibria)<sup>8</sup>, and Sander 2023<sup>1</sup>:

Table 9.2. Temperature-dependent Henry's Law constants for isoprene

Temperature	$k_H$ [mol·kg <sup>-1</sup> ·bar <sup>-1</sup> ]	Notes
25 °C (298 K)	0.013-0.028	Typical values; slight variation by source
30 °C	~0.025	Interpolated; temperature dependence
40 °C	~0.020	Higher temperature shifts equilibrium to gas

Temperature dependence is given by:

$$\ln \left( \frac{H(T_2)}{H(T_1)} \right) = - \frac{d \ln k_H}{d(1/T)} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

For isoprene,  $d \ln k_H / d(1/T) \approx 2000$  K (typical for moderately soluble compounds), giving moderate temperature dependence.

## B.2 Solubility and Saturation

Solubility of isoprene in water at 25 °C: ~600 mg·L<sup>-1</sup> or ~8.8 mmol·L<sup>-1</sup> (from literature and NIST data).

At 30 °C, solubility is slightly lower: ~550 mg·L<sup>-1</sup>.

Saturation concentration in water:

$$c_{\text{sat}} = \frac{\text{solubility (mg/L)}}{M_{\text{iso}} \text{ (g/mol)}} \times 1000 = \frac{600}{68.12} \times 1000 \approx 8.8 \text{ mmol/L}$$

## B.3 Henry's Law interpretation at ppm levels

At 100-500 ppm gas-phase isoprene (1 atm total pressure, 25 °C):

Table 9.3. Aqueous isoprene concentration at ppm-level gas concentrations

ppm	$p_{\text{iso}}$ (bar)	$c_{\text{aq}}$ via Henry (mg·L <sup>-1</sup> )	Fraction of saturation
100	$1.0 \times 10^{-4}$	~0.09	0.015 %
300	$3.0 \times 10^{-4}$	~0.27	0.045 %
500	$5.0 \times 10^{-4}$	~0.44	0.073 %

**Conclusion:** Even at the highest ppm levels (500 ppm), dissolved isoprene is far below saturation; water cannot significantly buffer or deplete the gas phase. The buffering effect reported in earlier analyses (where 99% was dissolved) applied to a *closed-system* scenario with large water volume (1 L) and small headspace (0.5 L) at high partial pressure (0.01 bar, equivalent to  $\sim 10,000$  ppm). In continuous open-loop operation at 100-500 ppm, Henry's law predicts negligible dissolution.

#### **B.4 Time to equilibrium**

In a continuous bubbler setup ( $100 \text{ mL}\cdot\text{min}^{-1}$  gas, 1 L water), the residence time is  $\sim 10$  minutes. However, mass transfer kinetics (bubble contact area, diffusion) determine actual approach to equilibrium, which may take 30-60 minutes or longer depending on mixing and temperature. In steady-state continuous operation, instantaneous equilibrium is never fully reached; instead, a dynamic balance emerges where production, stripping, and dissolution rates balance.

#### **B.5 Recommendations for measurement and calibration**

1. **Dry calibration first:** Inject known quantities of isoprene gas into a dry flask (30-40 °C) and verify detector (QGA/PID/GC) response against theoretical ppm values. This establishes the baseline system response free of partitioning effects.
2. **Systematic complexity:** Then add components one at a time (tubing, water contact, temperature variation) and observe how each affects signal. This isolates and quantifies partitioning losses if any occur.
3. **For production systems:** Account explicitly for partitioning in mass balance calculations. At low ppm levels, Henry's law predicts minimal dissolved isoprene, so most product remains in gas; however, any water contact should still be explicitly tracked.

**Temperature optimization:** Consider raising temperature to 40 °C (within growth tolerance) to shift equilibrium further toward the gas phase and improve detection sensitivity, as done in Uppsala headspace protocols.

## 9.3. Appendix C: Dew point and vapour pressure of isoprene

### C.1 Antoine constants for isoprene

Two Antoine correlations are in use, each valid in a specific temperature range:

**Ambient range (17-34 °C):**

$$\log_{10} P_{\text{sat}} = 3.21586 - \frac{706.92}{T + (-87.046)}$$

where  $P_{\text{sat}}$  is in mmHg and  $T$  is in °C.

Source: Osborn & Douslin<sup>18</sup>

**Cryogenic range (-57 to -38 °C):**

$$\log_{10} P_{\text{sat}} = 6.00474 - \frac{1179.217}{T + 219.726}$$

Source: Gubkov et al.<sup>19</sup>

For ppm-level dew-point calculations (which always fall in the -40 to -60 °C range for 50-500 ppm at 1 atm), **use the cryo correlation only.**

### C.2 Dew point as a function of gas-phase ppm

At 1 bar total pressure, the dew point (temperature at which condensation begins) is:

*Table 9.4. Dew point temperature as a function of gas-phase isoprene concentration*

ppm	Partial Pressure (mmHg)	T_dew (°C)*
50	0.0385	-60.8
100	0.0770	-54.1
150	0.1155	-49.9
300	0.2310	-42.2
500	0.3850	-37.0

\*These dew points are based on extrapolated literature correlations and have not been experimentally validated for isoprene; they are used only to indicate the approximate temperature regime where equilibrium condensation would start.

**Practical implication:** At bioreactor off-gas conditions (100-150 ppm, 25 °C ambient), isoprene is far above its dew point and remains fully gaseous. Hence condensation requires cooling to  $-45$  to  $-55$  °C and any measurable amounts are detected at moderate cooling ( $-5$  to  $-10$  °C) this can be explained by that kinetic nucleation can initiate droplet formation but in general, equilibrium condensation is negligible.

## 9.4. Appendix D: Evaluation of desorption experiments

$\dot{v}$  = volumetric flow [ $m^3 s^{-1}$ ]

$n_i$  = moles of isoprene in solution [mol]

$n_{sol}$  = moles of solvent [mol]

$x_i = \frac{n_i}{n_i + n_{sol}} \approx \frac{n_i}{n_{sol}}$  mol fraction isoprene in solution

$p_i$  = partial pressure of isoprene [Pa]

$p_{tot}$  = total pressure [Pa]

$K = \frac{x_i}{p_i}$  partitioning coefficient (Henry's constant as  $x_i \rightarrow 0$ ) [ $Pa^{-1}$ ]

$R$  = gas constant [ $J mol^{-1} K$ ]

$T$  = temperature of the volumetric flow  $\dot{v}$

Differential mass balance on mol basis:

Out flow of isoprene in gas phase + Change in amount of isoprene in solution = 0

$$\frac{p_i \dot{v}}{RT} dt + dn_i = 0 \quad [mol]$$

Before integration the amount of substance  $n_i$  in solution is related to the measured gas phase concentration of isoprene, assuming equilibrium is reached with a partitioning coefficient  $K$ .

$c_i$  = isoprene concentration in gas phase [ppm]

$p_i = p_{tot} \cdot c_i \cdot 10^{-6}$

Assuming  $n_i \ll n_{sol}$  the partitioning can be expressed as:

$$\begin{aligned} x_i = K \cdot p_i &\Rightarrow \frac{n_i}{n_{sol}} = K \cdot p_{tot} \cdot c_i \cdot 10^{-6} \Rightarrow n_i \\ &= n_{sol} K \cdot p_{tot} \cdot c_i \cdot 10^{-6} \end{aligned}$$

Substitution into the mass balance:

$$\frac{p_{tot} \cdot c_i \cdot 10^{-6} \dot{v}}{RT} dt + n_{sol} K \cdot p_{tot} \cdot 10^{-6} dc_i = 0$$

Separation of variables and integration yields a linear first-order rate dependency:

$$\frac{\dot{v}}{RT \cdot n_{sol} \cdot K \cdot 10^{-6}} \int_0^t dt = \int_{c_{i,t=0}}^{c_i} \frac{1}{c_i} dc_i$$

$$\ln(c_i) = \frac{\dot{v}}{RT \cdot n_{sol} \cdot K \cdot 10^{-6}} \cdot t + \ln(c_{i,t=0})$$

Plotting the logarithm of the off-gas concentration vs. time makes it possible to evaluate the partitioning constant K from the slope. Note that K becomes Henry's constant at very low amounts of isoprene, and that the unit of the constant can be recalculated as found appropriate. The intercept yields the initial isoprene concentration in gas phase and simply depends on the initial amount of isoprene added to the desorption experiment.

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