

INTRODUCTION

Direct air capture (DAC) is a promising approach not only for reducing our historical carbon footprint, but also for producing carbon-neutral fuels from CO_2 and water drawn directly from the atmosphere. First, the captured water is split into hydrogen (H_2) and oxygen (O_2) through electrolysis. The hydrogen then reacts with the captured CO_2 via the reverse water-gas shift reaction to form carbon monoxide (CO). A $CO-H_2$ mixture, known as syngas, can be converted into a variety of products, including boat and aviation fuels, through Fischer-Tropsch synthesis. Because these fuels are derived from atmospheric CO_2 , their combustion does not increase net carbon emissions, creating a closed carbon loop.



ZEOLITES

Zeolites are crystalline microporous aluminosilicates with high surface area, capable of adsorbing CO_2 from air due to their selective pore structures. CO_2 is held on the internal surfaces of the zeolite by physical adsorption (Van der Waals and electrostatic forces).

Ambient humidity significantly impacts zeolite performance. Water competes with CO_2 for adsorption sites, greatly reducing CO_2 uptake capacity. This issue can be mitigated by drying the air prior to adsorption.

Zeolites typically have a fast adsorption kinetics and are regenerable via heating or vacuum, making them good candidates for cyclic CO_2 capture processes.

The Si/Al ratio is a critical factor in zeolite synthesis, as it dictates the type of framework that can form under specific conditions. Zeolites with low Si/Al ratios, typically, between 1 and 5 are characterized by high cation density, which enhances their ion-exchange and adsorption capacities, making them particularly effective for direct air capture applications. This can be seen from the results of the experiments in the following section, where the 3 commercial zeolites under study had a Si/Al ratio between 1.15 – 1.4.

The volcanic ash under study from La Palma is characterized by its high aluminosilicate content, with significant impurities like Fe_2O_3 , Na_2O , and CaO . Its composition allows transformation into zeolites, specifically types X and sodalite, through alkaline fusion followed by hydrothermal synthesis.

With a Si/Al ratio of approximately 2.49, the volcanic ash under study is well-suited for the formation of low-silica zeolites. These zeolites are characterized by relatively high aluminum content, which translates to a high density of cation exchange sites. This makes them strongly hydrophilic, with excellent ion-exchange capacities and strong adsorption properties for molecules such as water and CO_2 .

In the following section CO_2 capture was tested for 3 different commercial zeolites. Ambient air was passed through a zeolite-packed column. CO_2 from air was adsorbed onto the zeolite, then desorbed by heating to produce a concentrated CO_2 stream.

DIRECT AIR CAPTURE EXPERIMENTS WITH ZEOLITES

During the adsorption process, graphs like the one shown in **Figure 1** are obtained. In these graphs, C_{0,CO_2} represents the inlet concentration of CO_2 . To calculate the total amount of CO_2 adsorbed (Q_{ads,CO_2}) the following equation is used:

$$Q_{ads,CO_2} = F \int_{t=0}^{t=t_{sat}} (C_{0,CO_2} - C_{CO_2}) dt$$

F represents the volumetric flow rate of air passing through the molecular sieves. C_{CO_2} corresponds to the CO_2 concentration after passing through the packed bed of zeolites, indicating the CO_2 that remains unadsorbed. The time at which the adsorption process reaches saturation, t_{sat} , represents the point at which the adsorbent material can no longer effectively capture CO_2 , serving as the upper limit of integration.

2 types of experiments were carried out with the 3 different types of commercial zeolites:

Experiment n°1: In these experiments, 4 TSA (temperature swing adsorption) cycles were performed using a packed bed of 40g of each zeolite. Adsorption occurred under ambient conditions, obtaining graphs like **Figure 2**, while desorption was induced through a temperature swing from ambient temperature to 310–315°C, obtaining graphs like **Figure 3**. **Figure 4** illustratively compares the CO_2 uptake, H_2O uptake, and H_2O/CO_2 selectivity for each 40 g packed bed of zeolites across all 4 cycles.

Experiment n°2: The adsorption and desorption behavior of the 3 zeolites were evaluated following a 12-day thermal pre-treatment at 100°C, aiming to stabilize their properties before one TSA cycle.

These experiments identified zeolites JLPM3 as the best candidate due to its superior overall CO_2 uptake, and 100°C as the preferred desorption temperature for the zeolites. At this temperature, all H_2O content is effectively liberated, 70-80% CO_2 adsorbed is desorbed, and performance is maintained over each successive cycle without degradation.

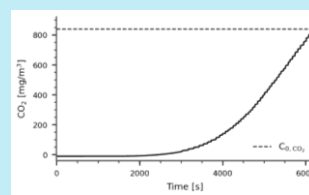


Figure 1. Experimental breakthrough curve for CO_2 adsorption.

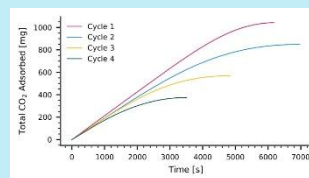


Figure 2. Total CO_2 adsorbed for each cycle during experiment n°1 as a function of time for a 40g packed bed of zeolites JLPM3.

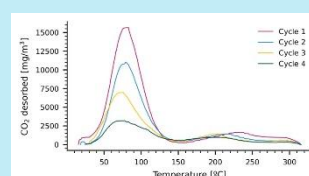


Figure 3. CO_2 desorption on each cycle during experiment n°1 as a function of temperature for a 40g packed bed of zeolites JLPM3.

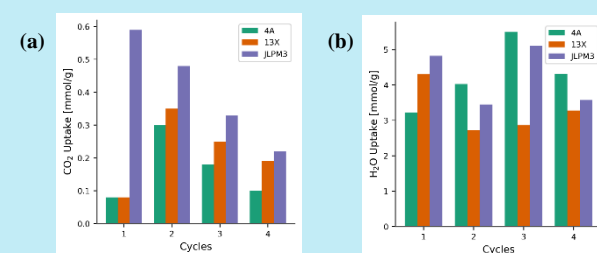


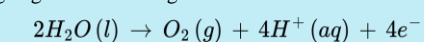
Figure 4. (a) CO_2 uptake comparison for 40g packed beds zeolites JLPM3, 13X and 4A for each cycle during experiment n°1. (b) H_2O uptake comparison for 40g packed beds of zeolites JLPM3, 13X and 4A for each cycle during experiment n°1.

GREEN HYDROGEN

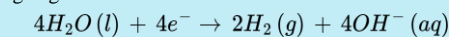
Water electrolysis is a process used to split water molecules into hydrogen and oxygen gases using an electric current. In the context of green hydrogen production, the electricity must come from a renewable source (solar, wind, etc.), this process is considered a clean and sustainable method for generating hydrogen gas.

Water electrolysis requires an electrolyzer, which consists of two electrodes - an anode and a cathode - submerged in water. The electrodes are made of conductive materials, such as metals or metal oxides. When an electric current is passed through the water; the following reactions occur:

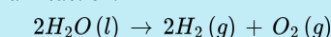
At the anode: Oxidation reaction takes place, generating oxygen gas and releasing electrons.



At the cathode: Reduction reaction occurs, producing hydrogen gas.



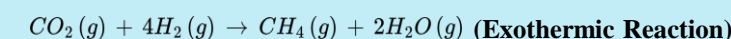
Overall reaction:



REVERSE WATER-GAS SHIFT REACTION

Reverse water-gas shift (RWGS) involves the reaction of CO_2 and H_2 to form CO and water: $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$

Due to the endothermic nature of this reaction, elevated temperatures are necessary to achieve better equilibrium conversions of CO_2 . Lower temperatures would result in the occurrence of undesired side reactions such as the Sabatier reaction:



Thermodynamic equilibrium suggests that achieving a good balance of CO_2 conversion and CO selectivity demands temperatures higher than 600 °C, as lower temperatures would result in high CO_2 conversions but much lower CO selectivity.

In the previous decade, several metal-based and metal oxide-supported catalysts have been rigorously studied. It has been established that noble metals (e.g., Pd, Pt, Ru, and Au) and transition metals (e.g., Cu, Ni, and Mo) are active for the RWGS reaction, but with differing activity and selectivity towards CO. When CO has a strong interaction with the catalyst, the C-O bond tends to dissociate and promotes the formation of C-H bonds, thereby leading to the methanation reaction. On the other hand, when CO has a weak interaction with the active site, it may either desorb or form aldehydes or alcohols. Transition metals with high CO adsorption such as Pt, Pd, Ru, Ni, and Rh are thus known to produce CH_4 as a side product and are also used to catalyze methanation reactions, while metals with low CO adsorption energy such as Cu, Au, and Ag are known to be selective to CO and are also used for methanol production.

Furthermore, the CO produced by RWGS, combined with green hydrogen from water electrolysis, constitutes syngas (a mixture of H_2 and CO), often used as a versatile feedstock for producing various fuels and chemicals.

PRODUCTS DERIVED FROM SYNGAS

1. Methanol (CH_3OH): $2H_2 + CO \rightarrow CH_3OH$ (Exothermic Reaction)

2. Synthetic Natural Gas (CH_4): $3H_2 + CO \rightarrow CH_4 + H_2O$ (Exothermic Reaction)

3. Fischer-Tropsch Hydrocarbons: $(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$ (Exothermic Reaction)

FISCHER-TROPSCH REACTION

Generally, the synthesis occurs at a pressure of 40-80 bar, with a cobalt or iron-based catalyst. The products obtained by the Fischer Tropsch synthesis process are governed by the Anderson-Schulz-Flory (ASF) distribution. It is highly essential to have a suitable catalyst in the process which has high selectivity towards jet range hydrocarbons. Cobalt has proved to be a suitable candidate when used with certain promoters, as has iron, albeit with generally lower selectivity. Low temperature FT (LTFT) synthesis is carried out in the temperature range of 200 to 240 °C using Fe or Co based catalysts. Alkenes are favored when Fe based catalysts are used at higher temperatures than Co based catalysts. On the other hand, high temperature FT synthesis is carried out in the range of 300 to 350 °C using Fe based catalysts. Aromatics are formed in significant quantities only in high temperature FT synthesis.

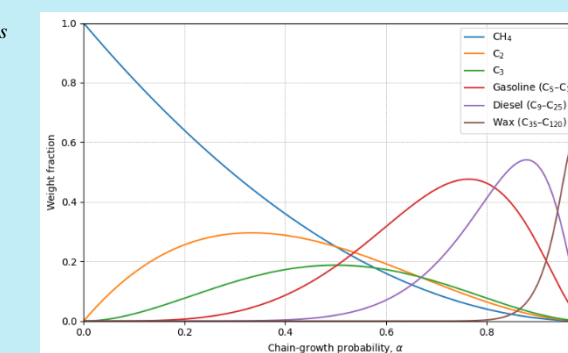
To determine the composition of the products as a function of the operating conditions at the reactor, the Anderson-Schulz-Flory (ASF) distribution has typically been used. The fraction of mass of the hydrocarbons i = number of C, and w_i depends on the probability of chain growth, α : $w_i = \alpha^{i-1}(1-\alpha)^2 \cdot i$

According to the studies by Song et al. (2004), α is a function of the temperature and the ratio CO-to- H_2 , as follows:

$$\alpha = \left(0.2332 \cdot \left(\frac{y_{CO}}{y_{CO} + y_{H_2}} \right) + 0.633 \right) \cdot (1 - 0.0039 \cdot ((T(^{\circ}C) + 273) - 533))$$

Figure 5 shows the effect of α on the composition of the products. Diesel is produced as the main component for values of α around 0.9 using LTFT. Gasoline requires slightly lower values of α , 0.7–0.8.

Figure 5. Product distribution as a function of chain length.



JET FUEL

The FT process produces a broad range of hydrocarbons, including a valuable fraction in the C8 – C16 range that corresponds to synthetic kerosene (the main component of jet fuel). These molecules can be separated via distillation of FT hydrocarbons.

The integrated pathway from direct air capture to synthetic jet fuels demonstrates a viable approach to carbon-neutral aviation. This technology closes the carbon loop: CO_2 emitted by aviation is re-harvested from the atmosphere and converted back into fuel, aligning with global climate goals. On the policy side, the European Union's ReFuelEU Aviation regulation mandates a minimum of 2% SAF (Sustainable Aviation Fuels) in aviation fuel blends starting in 2025, with a progressive ramp-up until 70% by 2050. This regulation highlights the growing demand for FT-based SAF and underscores its critical role in decarbonizing aviation in the coming decades.