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GlycoFoodChem



## WP3 - Avaliação de substâncias com potencial de mitigação de emissões de gases com efeito de estufa (GEE)

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# ▶ PRODUÇÃO DE METANO ENTÉRICO



Methanogenesis  $\longrightarrow$   $\text{CH}_4$   $\longrightarrow$  **loss of dietary energy along with contributing to greenhouse gas emissions**

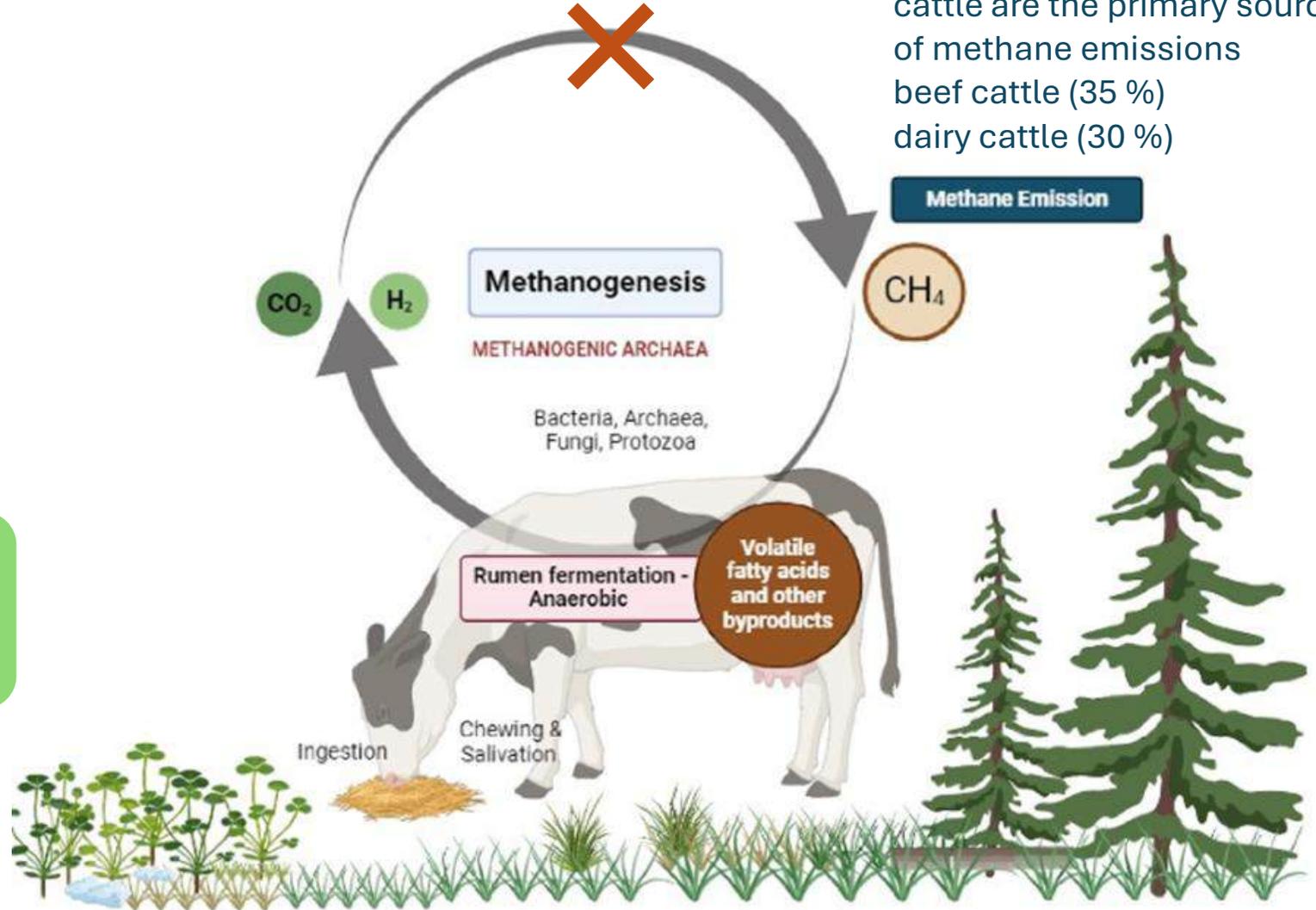
Methane emissions from ruminants cost farmers because of **feed's energy loss** (up to 12%, according to the FAO)

cattle are the primary sources of methane emissions  
beef cattle (35 %)  
dairy cattle (30 %)

fermentation end-products absorbed by the host animal



↓  $\text{CH}_4$  emissions  
↑ animal's productivity





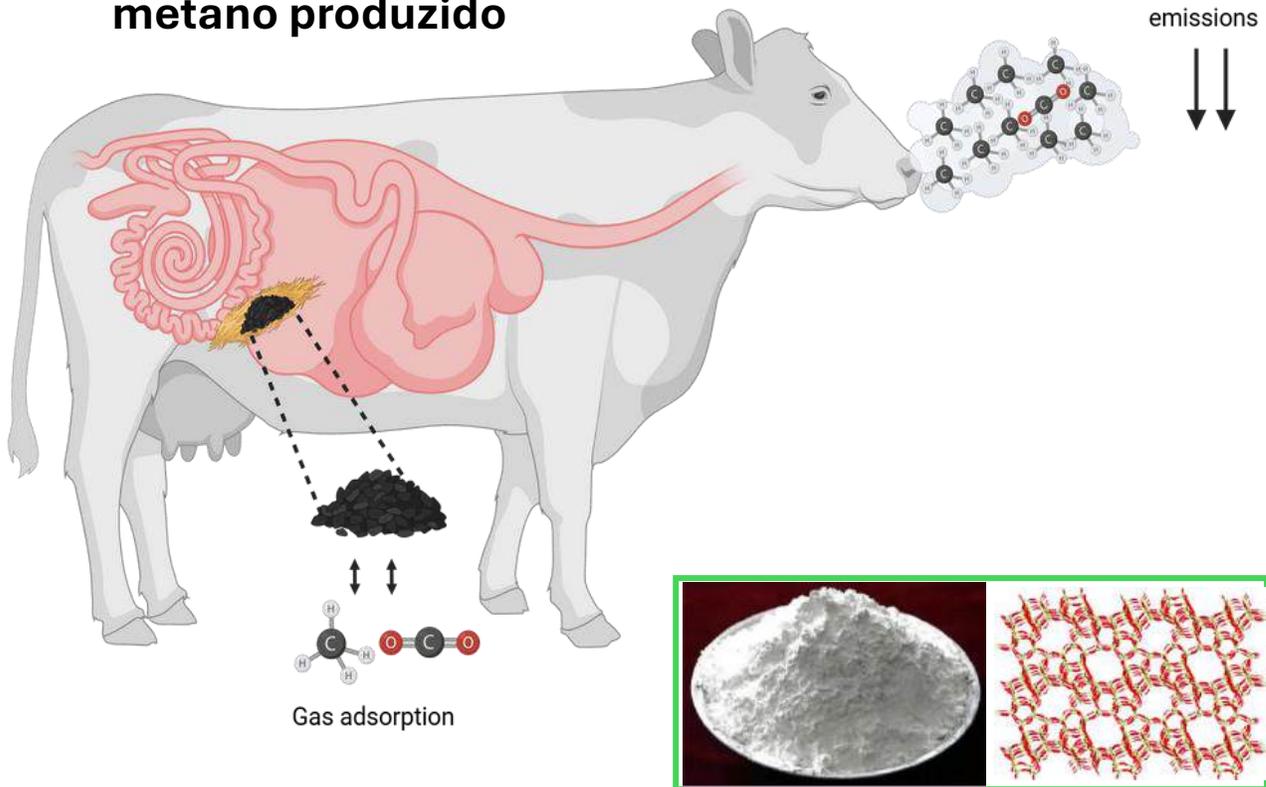
## Substâncias com potencial de mitigação

- 1) Moléculas pré-bióticas
- 2) Compostos carbonáceos
- 3) Compostos inorgânicos



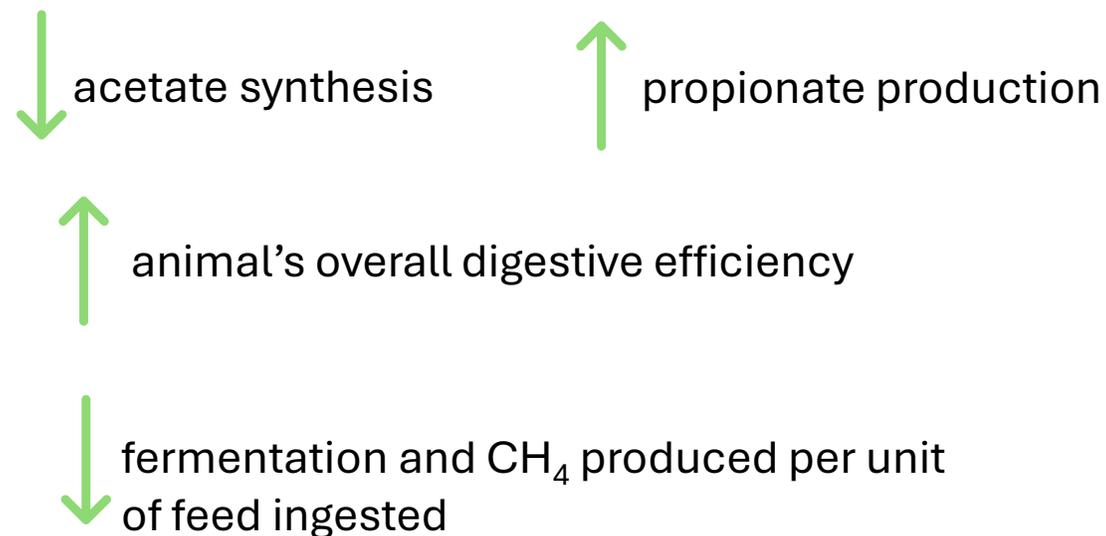
Obter de subprodutos agroalimentares substâncias com potencial poder de mitigação das emissões de metano

## Materiais que adsorvem o metano produzido



## Evitar a formação de metano

### Prebióticos



# ▶ BAGAÇO DE MAÇÃ COMO ESTRATÉGIAS PARA A REDUÇÃO DE METANO ENTÉRICO

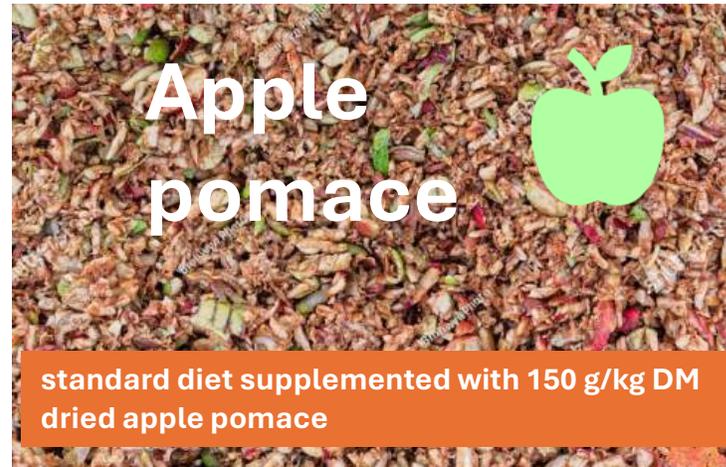


substantial increase in **propionate** and **butyrate** concentrations

Ruminal pH slightly increased;  
ammonia concentration decreased

significant **decrease** in total **protozoa** count

decline in **methane** emissions by 8%



**higher** nutrient **digestibility** and **milk production**

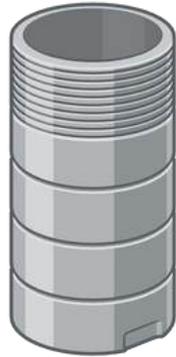
increase in total **ruminal SCFAs**

beneficial changes in ruminal **fatty acid profile**: higher unsaturated fatty acids and lower saturated fatty acids

# ▶ BAGAÇO DE MAÇÃ – OBTENÇÃO DE COMPOSTOS COM POTENCIAL DE MITIGAÇÃO



Compostos carbonáceos

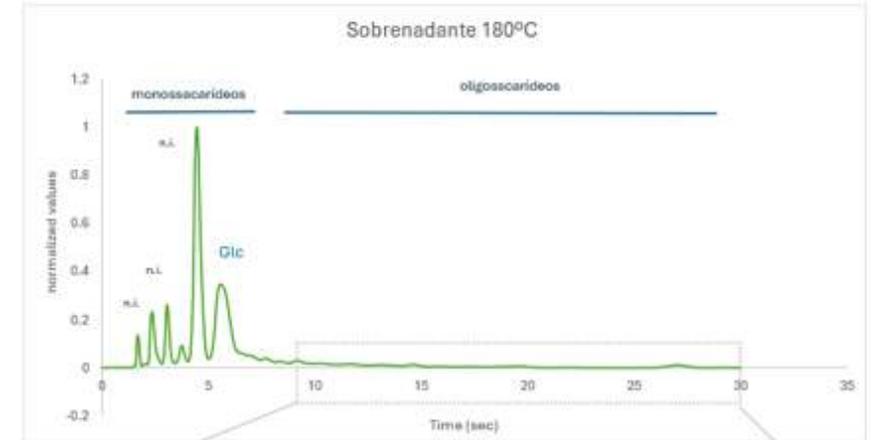


Carbonização/extração hidrotermal

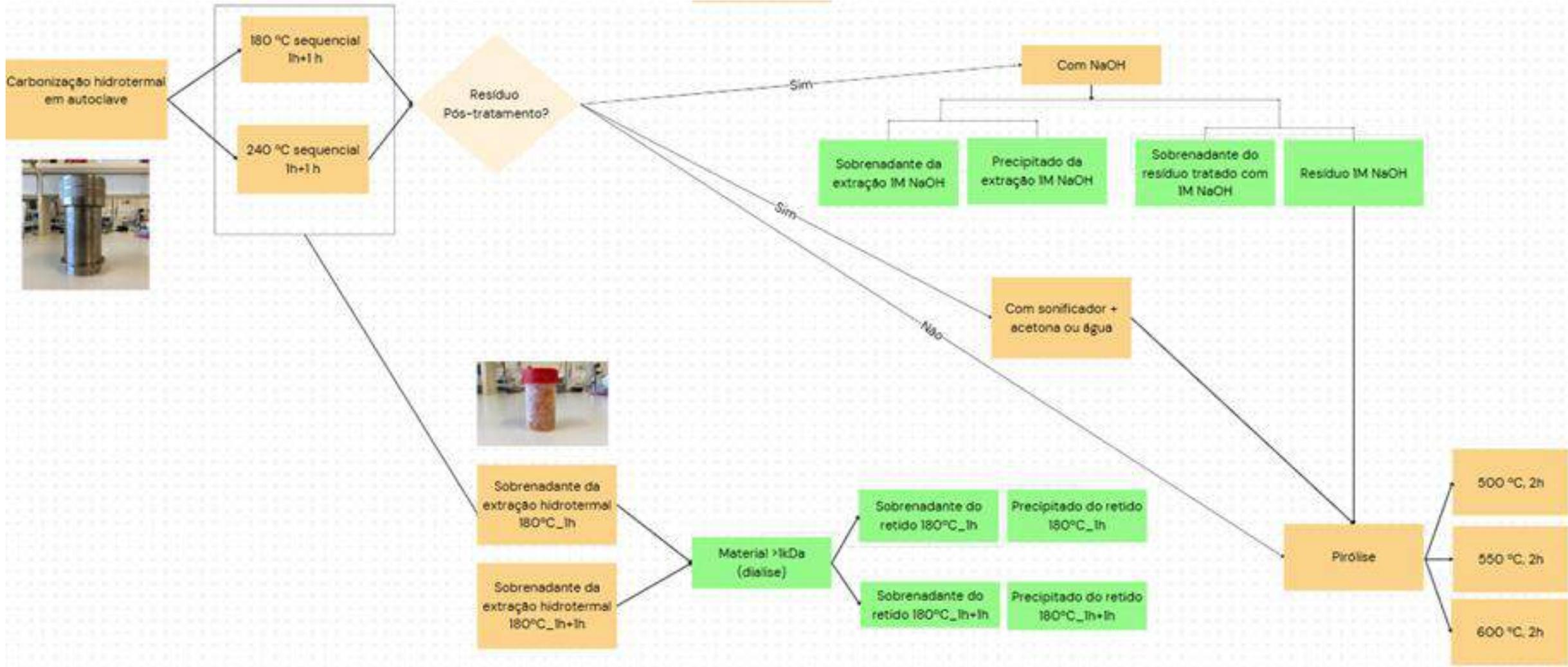


**Estratégia integrada para a obtenção de:**

- 1) Moléculas pré-bióticas (polissacarídeos e oligossacarídeos)
- 2) Compostos carbonáceos



# ► BAGAÇO DE MAÇÃ – OBTENÇÃO DE COMPOSTOS COM POTENCIAL DE MITIGAÇÃO



Flowchart of hydrothermal carbonization in autoclave, with the **recovery of molecules with possible prebiotic effects** and production of carbonaceous materials with possible capacity to mitigate greenhouse gases

# BAGAÇO DE MAÇÃ – OBTENÇÃO DE COMPOSTOS COM POTENCIAL PRÉBIÓTICO



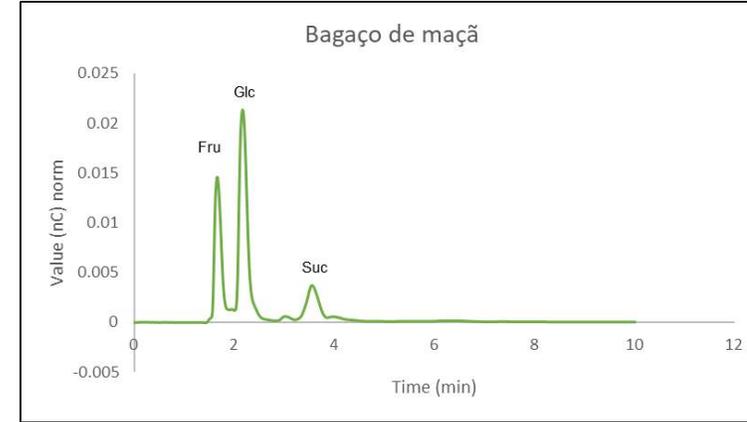
**Indumape**  
Industrialização de Fruta, S.A.

Monosaccharides

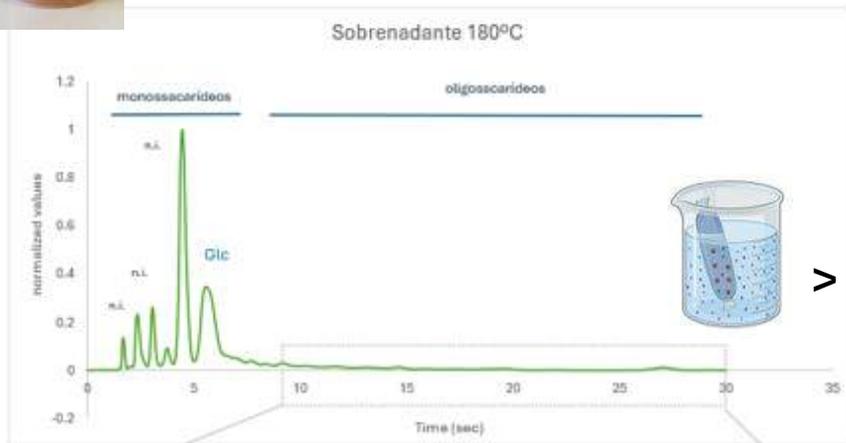
**AIR 80% ethanol**

Yeld (% mass)  
73.2%

Polysaccharides



**Hydrothermal 180°C**

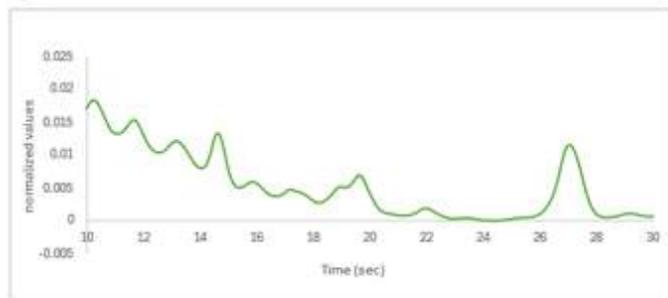


> 1 kDa material

Retentate (25-26%)

Precipitate

Supernatant



# ▶ BAGAÇO DE MAÇÃ – OBTENÇÃO DE COMPOSTOS COM POTENCIAL PRÉBIÓTICO



**Indumape**  
Industrialização de Fruta, S.A.

**AIR 80% ethanol**

Yeld (% mass)  
73.2%

				Sugar composition (% mol)								Total sugars (mg/g)
				Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA	
<b>Apple Pomace polysaccharides</b>				0.9	1.0	10.2	11.8	1.7	7.1	50.2	17.2	<b>742</b>
<b>Hydrothermal 180°C 1H</b>	<b>&gt; 1 kDa</b>	<b>Supernatant</b>		2.3	0	2	<u>18.7</u>	3.4	<u>16.9</u>	<u>21.6</u>	<u>35</u>	<b>953</b>
		<b>Precipitate</b>		1.3	0	0.6	<u>18.5</u>	0	<u>7.2</u>	<u>20.1</u>	<u>52.4</u>	<b>564</b>
<b>Hydrothermal 180°C 1+1H</b>	<b>&gt; 1 kDa</b>	<b>Supernatant</b>		2.9	0	0.8	<u>13.4</u>	1.6	<u>9.5</u>	<u>25.4</u>	<u>46.4</u>	<b>623</b>
		<b>Precipitate</b>		1.6	0	0	<u>13.6</u>	0	<u>10.1</u>	<u>32.1</u>	<u>42.6</u>	<b>452</b>
<b>Hydrothermal Residue 180°C</b>				0	0	1.0	<u>15.0</u>	3.0	2.0	74.3	4.6	<b>571</b>



**> 1 kDa material**

Retentate (25-26%)

Supernatant    Precipitate

**Alkaline extraction 1M NaOH**

# ► BAGAÇO DE MAÇÃ – OBTENÇÃO DE COMPOSTOS COM POTENCIAL PRÉBIÓTICO



Hydrothermal extraction Residue 180°C → Alkaline extraction 1M NaOH

Yield (% mass) 22.7		Sugar composition (% mol)							Total sugars (mg/g)	
		Rha	Fuc	Ara	Xyl	Man	Gal	Glc		UA
<b>1M NaOH</b>	<b>Supernatant 1M</b>									
	Supernatant	0	0	0	36	0.8	3.6	27.3	32.3	<b>472</b>
	Precipitate	0.1	0	1.4	59	1.5	3.5	27.5	7	<b>365</b>
	<b>Residue 1M</b>									
	Supernatant	0	0	0	0	0	0	0	100	<b>29</b>
	Residue	0	0	0.5	5	2.1	1.3	89.7	1.4	<b>821</b>

Xyloglucans and pectic polysaccharides

final residue of the alkaline extraction was enriched in cellulose

## ► BAGAÇO DE MAÇÃ – OBTENÇÃO DE COMPOSTOS COM POTENCIAL PRÉBIÓTICO

The fractions selected for the *in vitro* tests:

- Apple pomace
- Hydrothermal extract at 180°C (oligosaccharides and soluble polysaccharides)
- Hydrothermal Residue 180°C (Insoluble polysaccharides)
- 1M Alkali extract from Hydrothermal Residue 180°C (alkali soluble polysaccharides)

Samples tested *in vitro* tests:

Apple pomace

Grape pomace

Brewers Spent Grain

Standard feed formulations

Feed formulation with Apple pomace, Grape pomace, Brewers Spent Grain



DNA extraction, sequencing



**U. PORTO**



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**SCHOOL OF MEDICINE AND  
BIOMEDICAL SCIENCES**



- Materiais porosos (presença de micro e mesoporos)
- Elevada área superficial específica ( $\geq 300 \text{ m}^2/\text{g}$ )
- Não tóxicos



## 1ª Etapa

- **Carbonização hidrotermal** recorrendo à ação de pressão + temperatura.

Síntese hidrotermal usando proporção de 1:10 (10 g de bagaço para 100 mL de  $\text{H}_2\text{O}$ ), a **180 °C** ou **240 °C** com 2 etapas de 2 h.

## 2ª Etapa

- **Pirólises com patamar** de 30 min com extração dos óleos libertados.

Temperaturas: **500 °C**; **550 °C**; **600 °C**.



**Reator tubular horizontal**



Sample name	Specific Surface Area $A_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ )	Total Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ )	Mesopore Volume ( $\text{cm}^3 \text{g}^{-1}$ )
600 °C 30 min	44	0,04	0,047	0,032
550 °C 30 min	28	0,034	0,048	0,037
500 °C 30 min	21	0,016	0,032	0,025

- A melhor condição foi a 600 °C – 30 min, com: Área superficial: 44  $\text{m}^2/\text{g}$  e Volume total de poros: 0,047  $\text{cm}^3/\text{g}$ .
- As amostras produzidas apresentaram baixa área superficial e porosidade reduzida, limitando o seu uso direto para adsorção de gases.

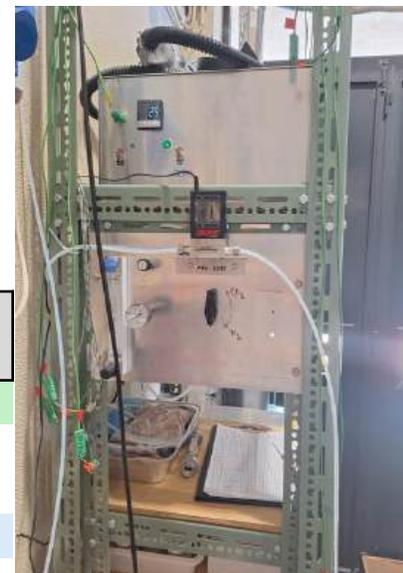
## Ativação do material?

# ▶ ATIVAÇÃO DE COMPOSTOS CARBONÁCEOS



- Pirólise até **700-800 °C**.
- Troca de N<sub>2</sub> para o gás de ativação escolhido (**CO<sub>2</sub>** ou **H<sub>2</sub>O**) durante **30 a 120 min** a temperatura constante.

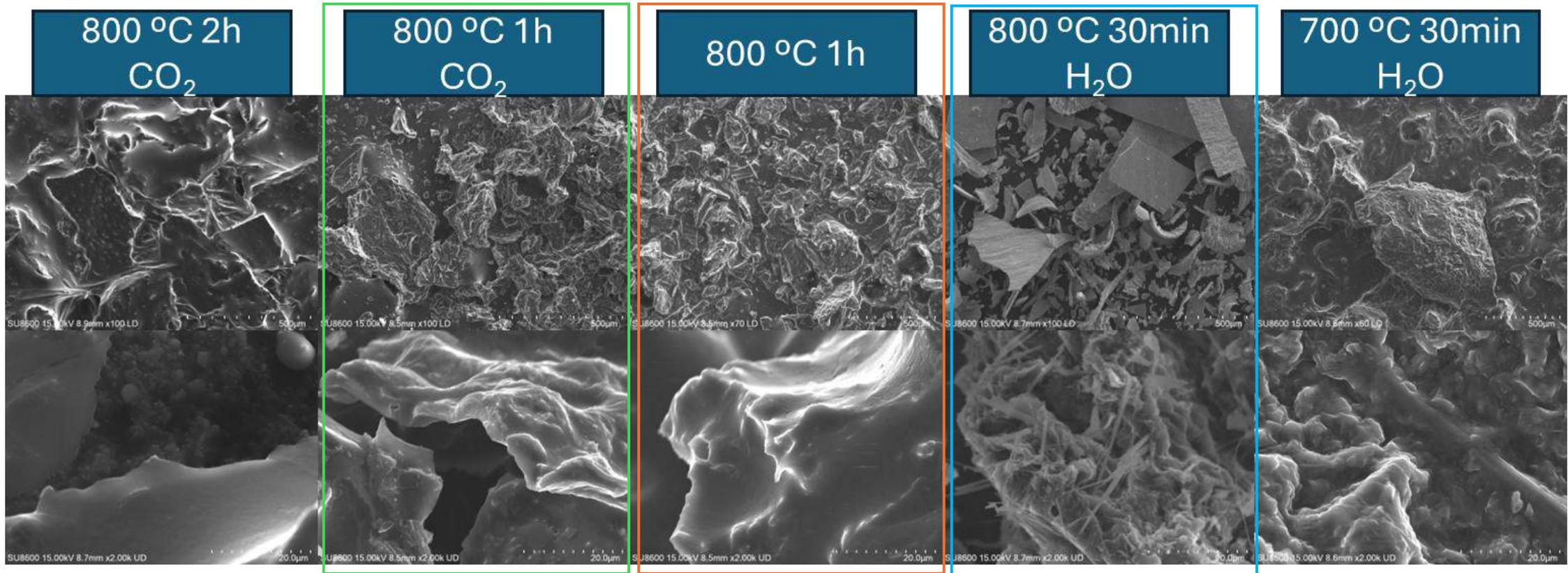
Caracterização Textural	Nome da amostra	Área Superficial Específica ABET (m <sup>2</sup> g <sup>-1</sup> )	Volume dos poros (cm <sup>3</sup> g <sup>-1</sup> )	Volume total dos poros (cm <sup>3</sup> g <sup>-1</sup> )	Volume dos Mesoporos (cm <sup>3</sup> g <sup>-1</sup> )
	800 °C 2h CO <sub>2</sub>	682	0.445	0.495	0.193
800 °C 1h CO <sub>2</sub>	552	0.376	0.431	0.2	
800 °C 30 min CO <sub>2</sub>	433	0.299	0.343	0.154	
800°C 30min H <sub>2</sub> O	618	0.384	0.438	0.184	
800 °C 20 min H <sub>2</sub> O	579	0.367	0.421	0.177	
800 °C 1h	72	0.081	0.097	0.08	
750 °C 1 h CO <sub>2</sub>	397	0.227	0.255	0.068	
750 °C 40 min H <sub>2</sub> O	352	0.227	0.260	0.128	
750 °C 30 min H <sub>2</sub> O	616	0.358	0.4	0.135	
750 °C 20 min H <sub>2</sub> O	484	0.289	0.332	0.118	
700 °C 30 min H <sub>2</sub> O	483	0.287	0.337	0.121	



Reator tubular vertical.

- A ativação com CO<sub>2</sub> e H<sub>2</sub>O aumentou significativamente a área superficial e porosidade dos materiais.
- A melhor amostra foi ativada com CO<sub>2</sub> a 800 °C durante 2 h.
- A ativação favorece formação de microporos e mesoporos.
- O biochar não ativado mostrou baixa área superficial e porosidade muito limitada.

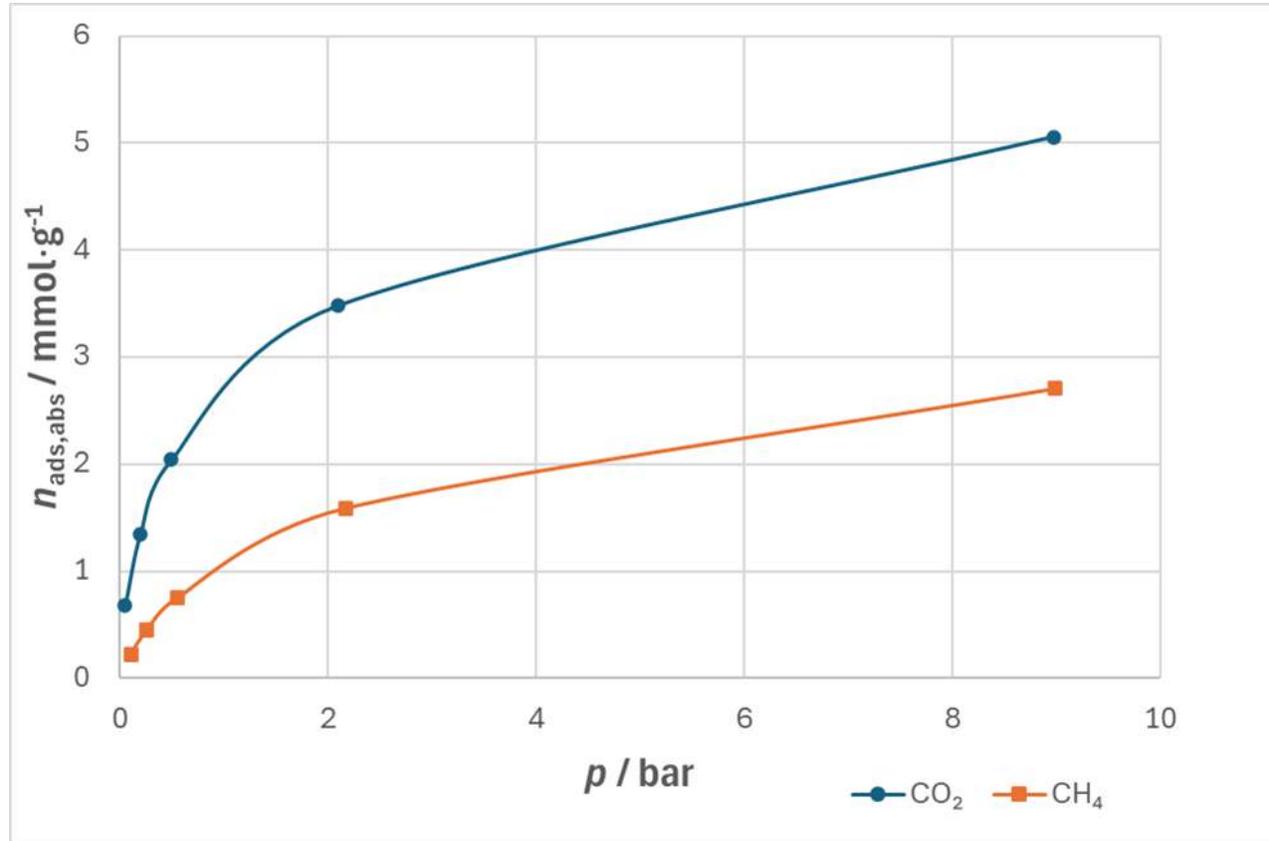
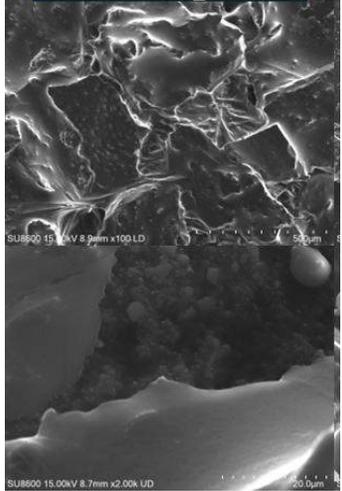
# ▶ ATIVAÇÃO DE COMPOSTOS CARBONÁCEOS - MORFOLOGIA



- A ativação com CO<sub>2</sub> e H<sub>2</sub>O aumenta a rugosidade e o desenvolvimento dos poros.
- A amostra não ativada apresenta superfície mais compacta e densa (pouco porosa).
- A amostra com H<sub>2</sub>O (800 °C, 30 min) mostra estruturas tipo agulhas, possivelmente resíduos minerais.

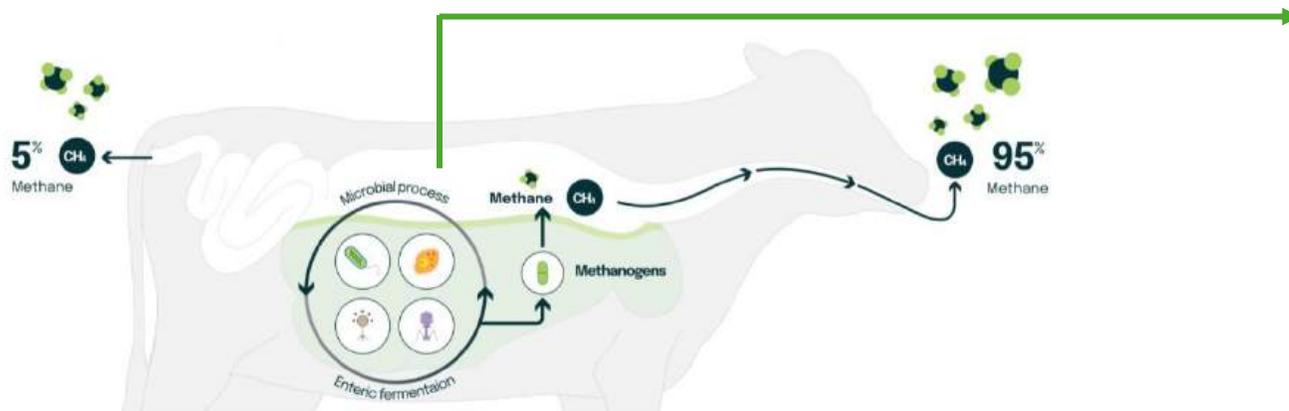


800 °C 2h  
CO<sub>2</sub>



- CO<sub>2</sub> adsorvido: 5,06 mmol/g.
- CH<sub>4</sub> adsorvido: 2,71 mmol/g.

- Adsorção eficaz a 25 °C e mesmo a baixa pressão.
- Material mostra forte afinidade por CO<sub>2</sub> (quase o dobro face ao CH<sub>4</sub>).



## → Main rumen air cavity gas composition

Gas	Average percentage (%)
Nitrogen	7.0
Methane	20-30
Carbon Dioxide	45-75

## → Physico-chemical properties of the main rumen gases

Molecule	$\sigma$ [Å]	$\alpha$ [Å <sup>3</sup> ]	$\mu$ [D]	$\Theta$ [D Å]
CO <sub>2</sub>	3.30	2.507	0.0	4.30
CH <sub>4</sub>	3.80	2.448	0.0	0.02
N <sub>2</sub>	3.64	1.710	0.0	1.54

$\sigma$ : kinetic diameter,  $\alpha$ : polarizability,  $\mu$ : dipole moment,  $\Theta$ : quadrupole moment

## Gas selectivity and affinity

- Hydrophilic materials will favour CO<sub>2</sub> capture over N<sub>2</sub> and CH<sub>4</sub>.
- Conflicting behaviour between N<sub>2</sub> and CH<sub>4</sub>, very complex separation in this system



Hydrophobic materials will most likely be favored overall.

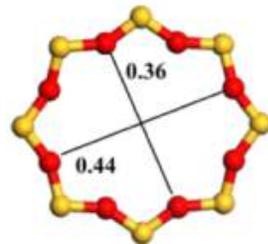


## Potential candidates- Zeolites

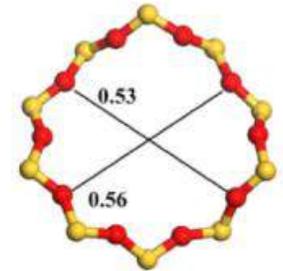
→ Thermal and chemical stability, high surface area, microporous structure and tunability → interesting candidates.

→ Hydrophobic siliceous zeolites → Composition:  $\text{SiO}_2$ , not hazardous for the animal

→ Both computational and experimental studies have found that smaller channels favour methane adsorption.



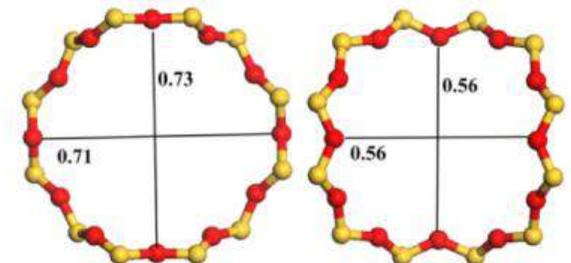
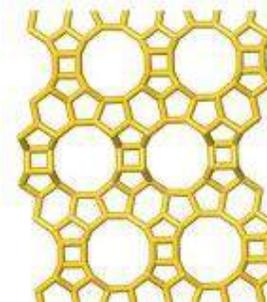
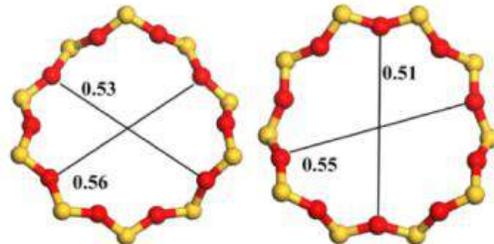
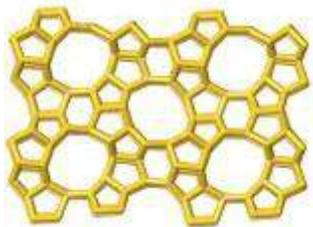
Around 0.35-0.54 nm diameter



Silicalite-1: Si/Al=750

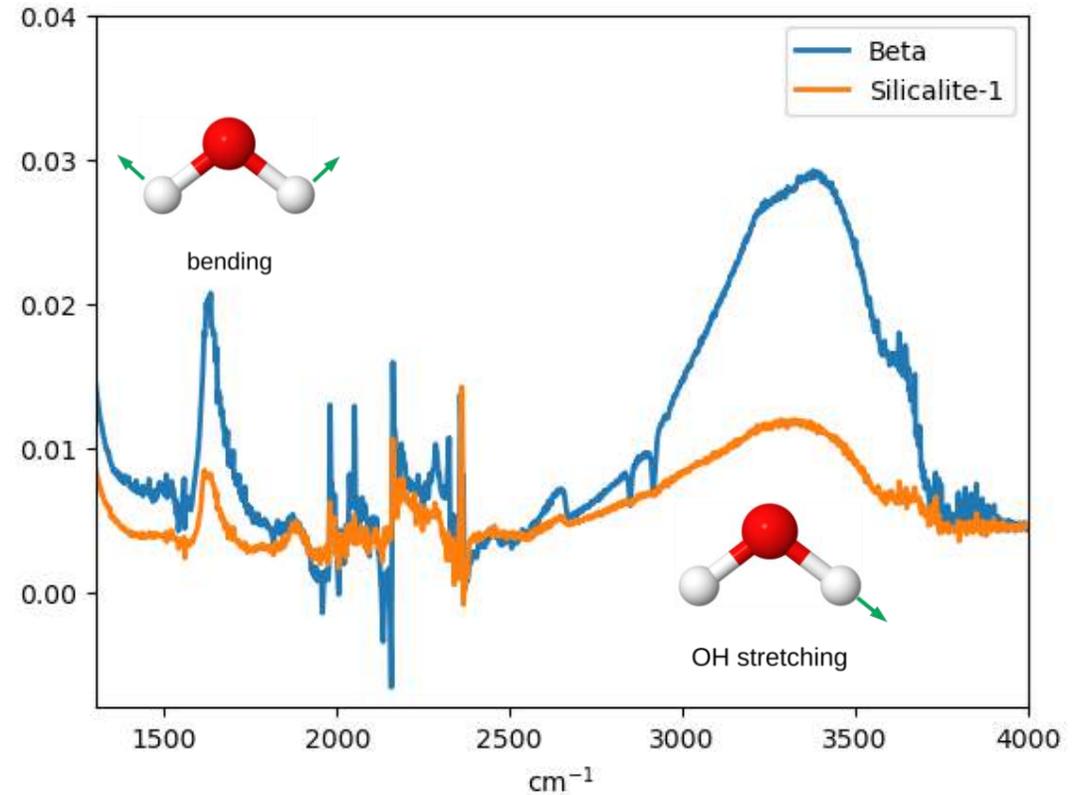
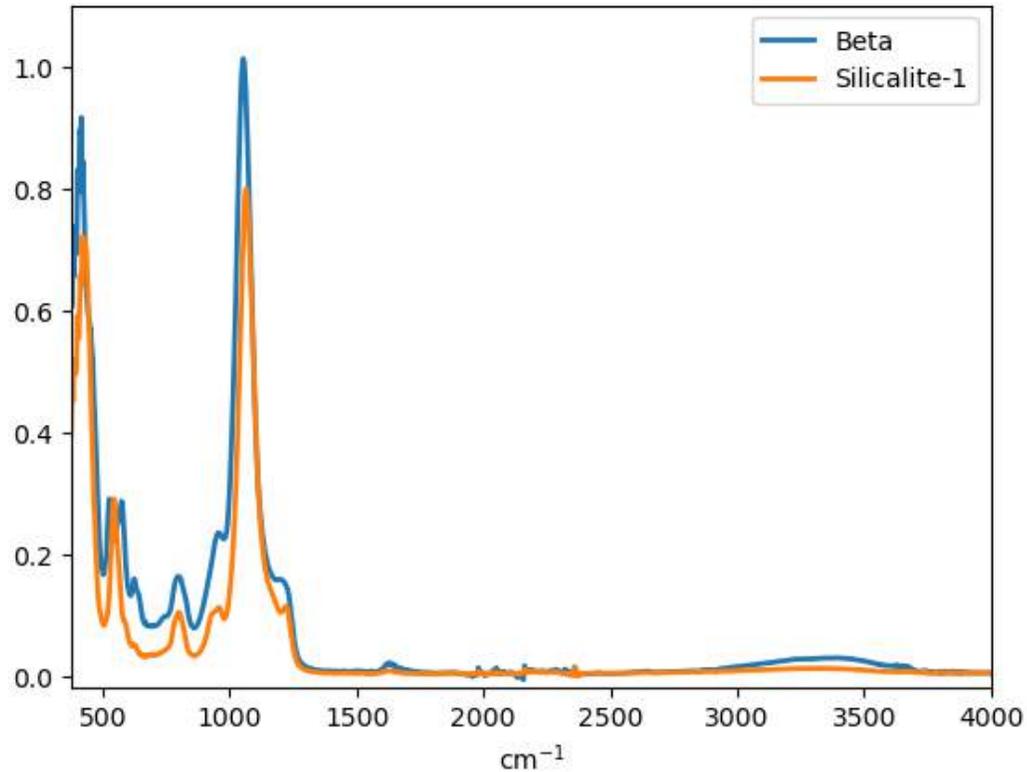
→ Selected high Si commercial zeolites

Beta: Si/Al=250





## FTIR



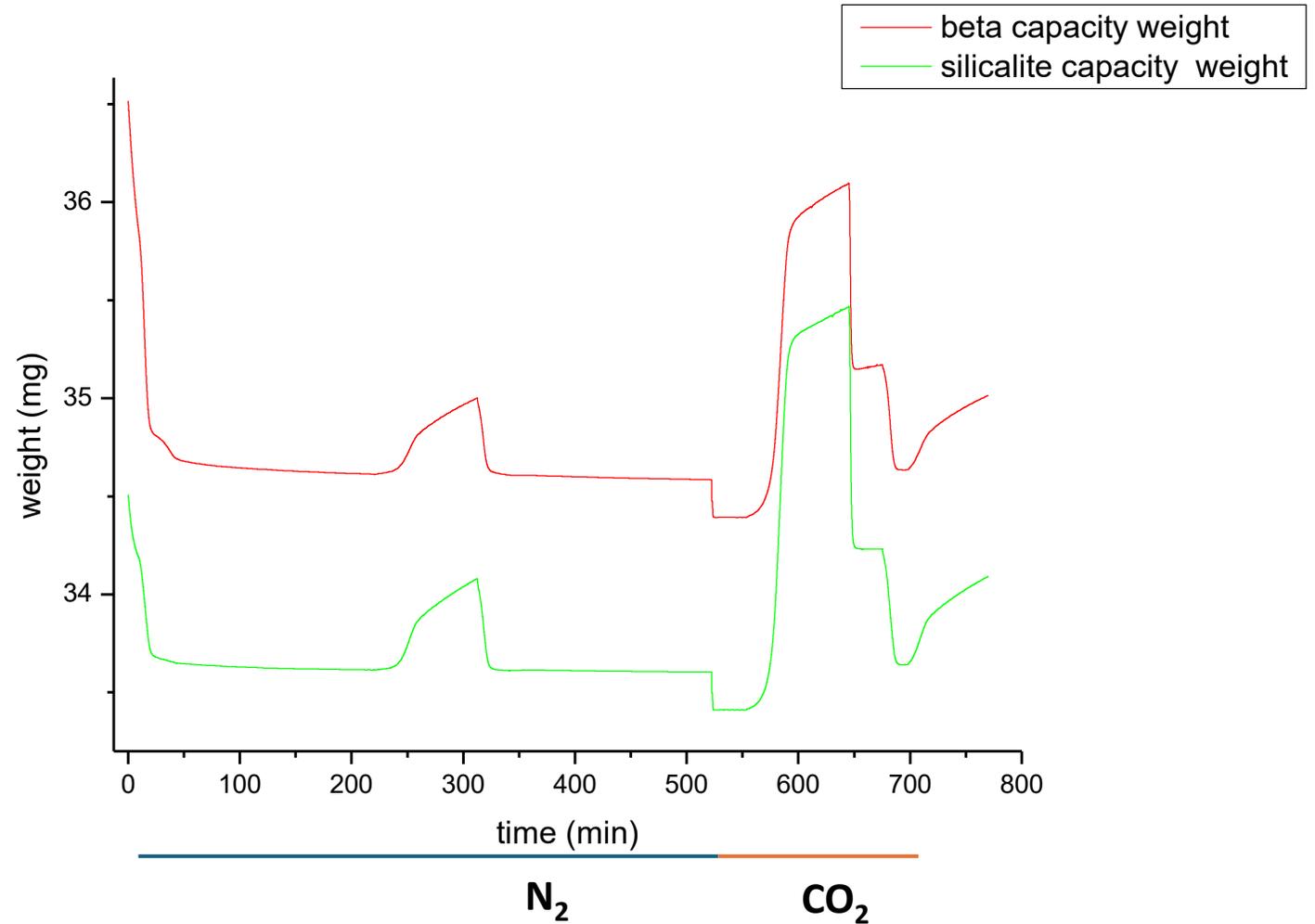
Silicalite-1 more hydrophobic than beta



- Thermogravimetric analysis was then attempted as a proxy uptake measurement.

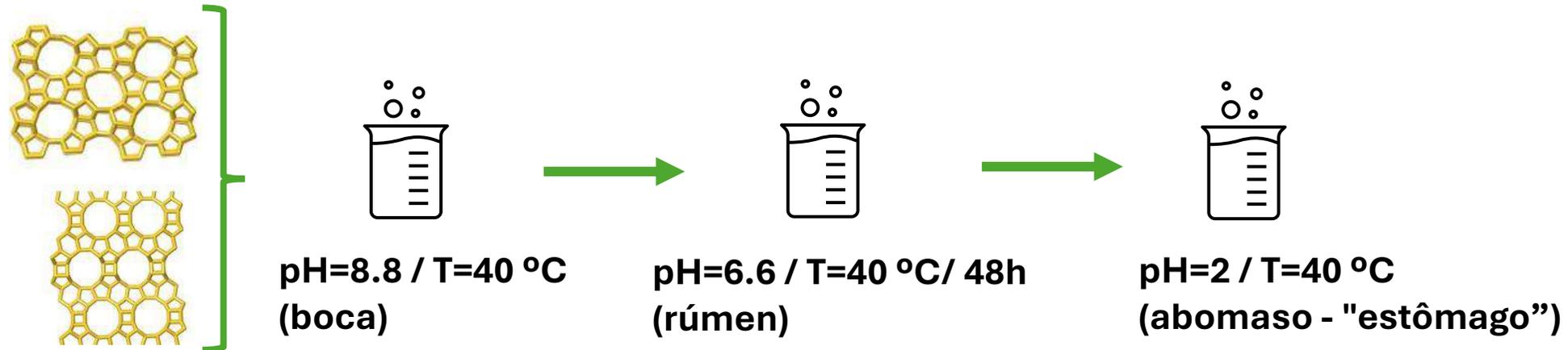
CO<sub>2</sub>/N<sub>2</sub> selectivity ≈ 2.8

Preference for CO<sub>2</sub> over N<sub>2</sub>





- Simulation the main digestive system characteristics, pH and temperature.



Check for degradation of their structure and performance.

- The next step would be to perform tests utilizing real rumen samples, not only to test stability, but also to simulate *in vivo* gas adsorption. Possible impact on microbiota.



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