

## RECOVERY OF MESOPOROUS SILICA AND VALUABLE CHEMICALS FROM THE RECYCLING OF SPENT SOLID CO<sub>2</sub> ADSORBENTS VIA CATALYTIC PYROLYSIS

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### ABSTRACT

We developed a technology for recycling spent solid CO<sub>2</sub> adsorbents comprised of mesoporous silica (Si) and polyethyleneimine (PEI) via catalytic pyrolysis. Spent Si-PEI adsorbent was pyrolyzed at 400-650 °C to thermally decompose the oxidized PEI and recover the silica. At ≥500 °C, near-complete degradation of PEI was achieved, and silica with a pore volume of ca. 1.2 cm<sup>3</sup>/g was obtained, about 70% of the virgin silica's pore volume. Characterizing the pyrolysis oils revealed the presence of alkylpyrazines, which are heteroaromatics compounds of commercial interest. A method based on gas chromatography was developed to quantify the alkylpyrazines, whose yield was determined to range from 1.7 wt.% at the lowest pyrolysis temperature to 4.9 wt.% at the highest. The upgrading of the PEI pyrolysis vapors with different catalysts was studied to maximize the alkylpyrazines; using a USY catalyst, an alkylpyrazine yield of 7 wt.% was achieved at a pyrolysis temperature of 600 °C. The recovered silica from the pyrolysis runs was successfully re-impregnated with fresh PEI and achieved 11.9 wt.% CO<sub>2</sub> adsorption capacity, only slightly lower than the 13.8 wt.% CO<sub>2</sub> adsorption capacity of a Si-PEI adsorbent made from virgin silica.

**KEYWORDS:** Recycling, Mesoporous silica, Pyrazines, CO<sub>2</sub> adsorbents, CO<sub>2</sub> capture

### INTRODUCTION

Carbon capture and storage (CCS) has emerged as a pivotal technology in the global strategy to combat climate change by mitigating carbon dioxide emissions from industrial sources and power generation. As countries worldwide strive to meet the ambitious targets set by the Paris Agreement, the European Union has specifically recognized CCS as an essential tool within its comprehensive climate change strategy to achieve carbon neutrality by 2050. By integrating CCS technologies, the EU aims to reduce existing CO<sub>2</sub> emissions and address emissions from hard-to-abate sectors, thereby ensuring a cleaner, sustainable future and reinforcing its leadership role in global climate policy initiatives. Amine scrubbing is the most mature CO<sub>2</sub> capture technology, having been adapted from separating CO<sub>2</sub> from natural gas. However, amine scrubbing has limitations, including high energy demand for regenerating the solvent and environmental problems such as volatile amine loss and reactor corrosion, which are not completely solved by using mixed amines rather than monoethyleneamine. These factors result in relatively high capture costs, which have catalyzed the development of alternative or second-generation technologies <sup>[1]</sup>.

The Solid Adsorbent Looping Technology (SALT) is a promising alternative CO<sub>2</sub> capture technology that utilizes strongly basic solid adsorbents, such as polyethyleneimine (PEI) supported on

**Table 1.** Elemental composition, pore volume, and volatile matter content of the spent Si-PEI and the parent mesoporous silica PQ3.

Sample	C, wt.%	H, wt.%	N, wt.%	S, wt.%	Pore volume, cm <sup>3</sup> /g	Volatiles, wt.%
Si-PEI	21.1	4.2	11.0	0.043	0.421	54.1
PQ3	0.0	0.7	0.0	0.022	1.754	0.0

**Table 2.** Properties of the catalysts used for upgrading the PEI vapors in this work.

Catalyst	BET surface area, m <sup>2</sup> /g	Micropore surface area, m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Micropore volume, cm <sup>3</sup> /g	Brønsted acid sites, μmol/g	Lewis acid sites, μmol/g	Basic sites, μmol/g
USY	188	129	0.235	0.037	8.8	14.4	-
ZSM-5	162	97	0.135	0.039	36.5	18.1	-
MgO	20	-	0.179	-	-	-	85.9
ZrO <sub>2</sub>	116	-	0.093	-	0.0	36.1	17.0
ZrO <sub>2</sub> /TiO <sub>2</sub>	85	-	0.349	-	7.9	81.4	12.2

mesoporous silica (Si-PEI). Si-PEI circulates between a reactor for the adsorption of CO<sub>2</sub> from industrial flue gases and a regenerator to release the adsorbed CO<sub>2</sub> and regenerate the adsorbent. During operation, PEI gradually oxidizes, loses CO<sub>2</sub> adsorption capacity, and eventually must be replaced with fresh adsorbent. The technology's commercial success depends on reducing the adsorbent replacement cost to <10€/ton CO<sub>2</sub> captured. One way to achieve this cost is by reducing the virgin mesoporous silica needed to produce Si-PEI adsorbents.

In this work, we developed a technology for the recycling of the spent Si-PEI adsorbent via pyrolysis to a) recover the mesoporous silica for reuse in the production of fresh Si-PEI and b) recover valuable chemicals from the thermal decomposition of PEI to generate additional revenue. The literature on chemical products from PEI pyrolysis is limited to only a couple of studies published in 1955<sup>[2]</sup> and 1975<sup>[3]</sup>. Barb reported high yields of piperazines from the pyrolysis of N-substituted ethyleneimine monomers at temperatures up to 280 °C<sup>[2]</sup>. On the other hand, Nedel'ko et al. reported the production of ammonia, ethylamine, pyrrole, and ethyl-pyrroles when pyrolyzing branched PEI, noting an absence of piperazine formation<sup>[3]</sup>.

## METHODOLOGY

The feedstock utilized was spent Si-PEI from previous work<sup>[4]</sup>, with its properties detailed in **Table 1**. The properties of the parent mesoporous silica (PQ3) that was impregnated with PEI to prepare the Si-PEI sample are also presented in **Table 1**. The catalysts used included a Y zeolite-based catalyst (USY), a ZSM-5 zeolite-based catalyst (ZSM-5), MgO derived from calcined natural magnesite, and ZrO<sub>2</sub> and ZrO<sub>2</sub>/TiO<sub>2</sub>, both acquired from Saint-Gobain. The properties of the catalysts are presented in **Table 2**. The textural properties were determined by nitrogen physisorption. The number and type of acid sites were measured by Fourier-transformed infrared spectroscopy coupled with *in situ* pyridine adsorption<sup>[5]</sup>. The number of basic sites was measured by temperature-programmed desorption of CO<sub>2</sub><sup>[6]</sup>.

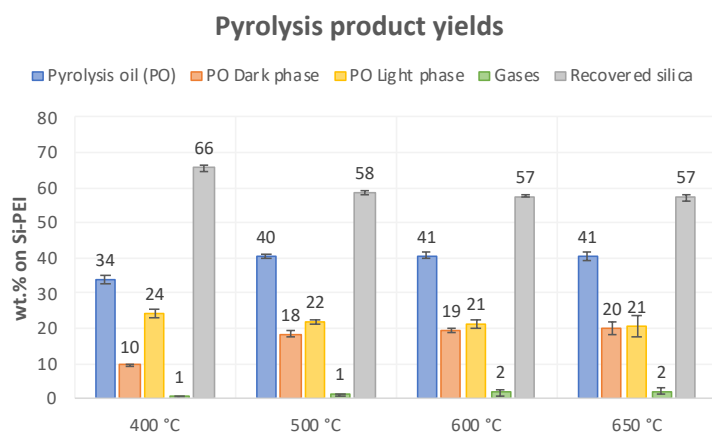
The pyrolysis of the Si-PEI was carried out in a bench-scale pyrolysis unit equipped with a fixed bed reactor, which has been described in detail in a previous work [7]. The reactor was loaded with 5 g of Si-PEI and a quantity of catalyst that depended on the target catalyst-to-feed ratio (C/F), which was varied between 0, 0.5, 1, 2, and 3. The catalyst was separated from the Si-PEI feedstock with a layer of quartz wool so that only the PEI pyrolysis vapors came in contact with the catalyst. All the pyrolysis products (liquid, gas, solid) were measured, and a complete mass balance was obtained (91-96%).

The pyrolysis gases were analyzed offline in a gas chromatograph (GC) equipped with a flame ionization detector and a thermal conductivity detector for the detection of CO, CO<sub>2</sub>, H<sub>2</sub>, and C<sub>1</sub>-C<sub>6</sub> hydrocarbons. The liquid products were weighed and analyzed by combustion in a LECO TruSpec Micro elemental analyzer for the determination of C, H, and N, by Karl-Fisher titration for the determination of water content, and by GC coupled with mass spectrometry (MS) for the qualitative determination of their chemical composition. A new method was developed for the quantitative determination of alkylpyrazines in the pyrolysis liquids by GC-MS and high-performance liquid chromatography (HPLC) with a diode array detector (DAD) [8]. The Si-PEI pyrolysis residue was analyzed by nitrogen physisorption to determine its textural properties.

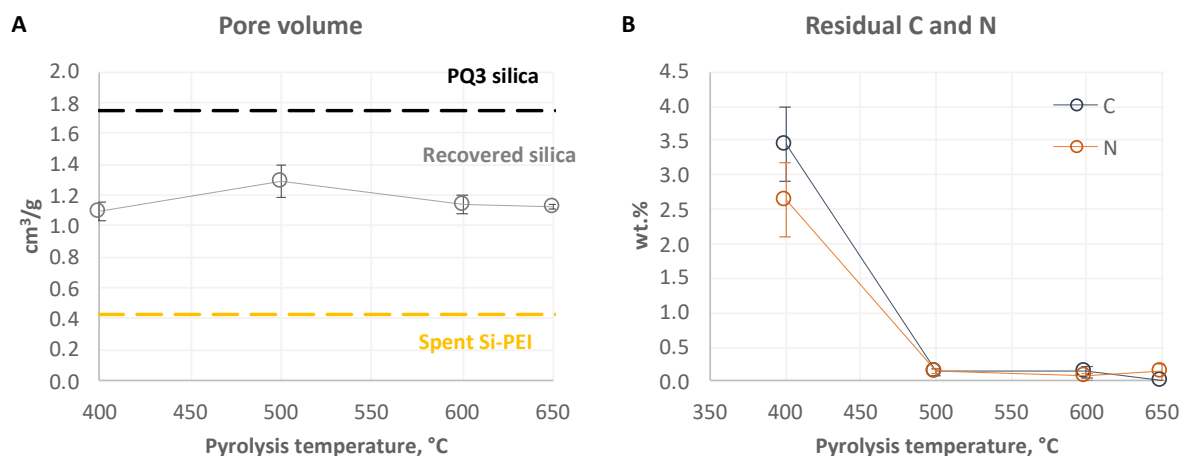
## RESULTS AND DISCUSSION

The pyrolysis of Si-PEI was initially carried out in the absence of a catalyst at temperatures 400, 500, 600, and 650 °C. The yields of the pyrolysis products are presented in **Error! Reference source not found.** as a function of the pyrolysis temperature. The main product at all temperatures was the Si-PEI residue (recovered silica), which was about 57-58 wt.% at temperatures  $\geq 500$  °C. The second most abundant product was the pyrolysis liquid, which ranged from 34 wt.% at 400 °C to 40-41 wt.% at 500-650 °C. The pyrolysis oil was comprised of two phases; a light-colored phase and a dark-colored phase. As the pyrolysis temperature increased, the yield of the dark phase increased from 10 wt.% to 20 wt.%, while the yield of the light phase decreased from 24 wt.% to 21 wt.%. The yield of the pyrolysis gases was very low in all cases and ranged between 1 wt.% and 2 wt.%.

One of this work's goals was to recover the mesoporous silica and reuse it as a substrate for re-impregnation with PEI to produce fresh CO<sub>2</sub> adsorbent. The primary property of the silica that determines the amount of PEI polymer that can be impregnated on it is its pore volume. The pore volume of the recovered silica from the non-catalytic experiments is presented in **Figure 2A** as a



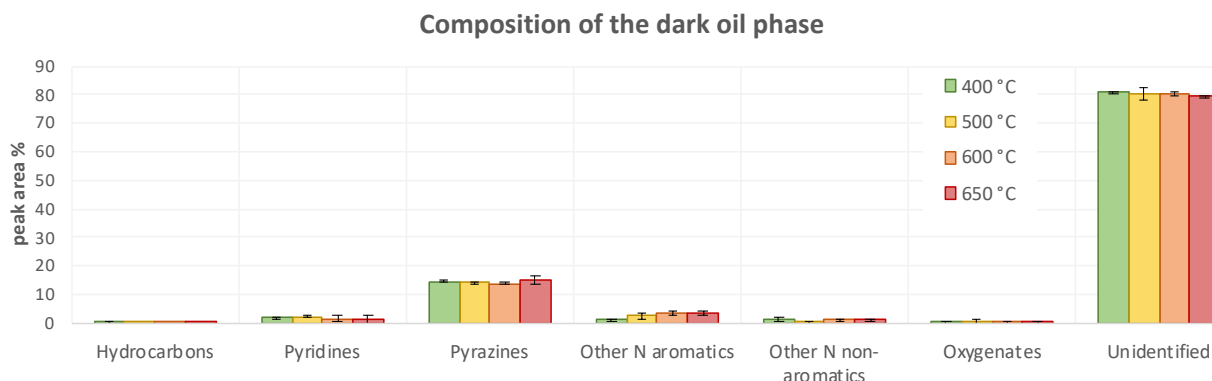
**Figure 1.** Pyrolysis product yields from the non-catalytic pyrolysis of Si-PEI at various temperatures.



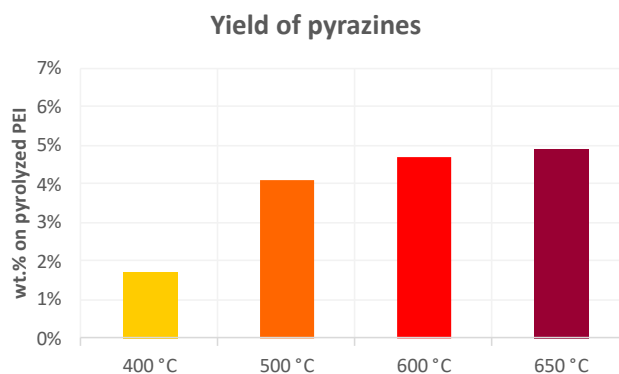
**Figure 2.** A) Pore volume of the spent Si-PEI, the PQ3 silica, and the recovered silica from the non-catalytic pyrolysis of spent Si-PEI as a function of the pyrolysis temperature. B) Residual C and N on the recovered silica as a function of the pyrolysis temperature.

function of the pyrolysis temperature and in comparison to the pore volume of the spent Si-PEI and the pore volume of the parent PQ3 silica. The pore volume of the spent Si-PEI was the lowest, 0.42 cm<sup>3</sup>/g, due to its pores being occupied by the spent PEI polymer. Pyrolysis of the spent Si-PEI led to the thermal decomposition and volatilization of the PEI polymer and the recovery of the pore volume to around 1.1 cm<sup>3</sup>/g. Considering the experimental error, the recovered pore volume was independent of the pyrolysis temperature. The residual C and N on the recovered silica are presented in **Figure 2B** as a function of the pyrolysis temperature. At the lowest pyrolysis temperature, a significant amount of C and N was still present on the recovered silica, indicating incomplete decomposition and removal of the spent PEI. However, at temperatures 500 °C or higher, only negligible amounts of C and N could be found on the recovered silica, indicating a near-complete removal of the spent PEI. The recovered silica (pore volume of ca. 1.2 cm<sup>3</sup>/g) was re-impregnated with PEI to produce fresh Si-PEI adsorbent, which was tested for its CO<sub>2</sub> adsorption capacity. The optimum PEI loading before agglomeration started to occur was 43 wt.%, only slightly lower than the optimum PEI loading of 47 wt.% that could be achieved on the virgin silica. At 43 wt.% PEI loading, the CO<sub>2</sub> adsorption capacity of the adsorbent made with recovered silica was 11.9 wt.%, slightly lower than the 13.8 wt.% CO<sub>2</sub> adsorption capacity of a Si-PEI adsorbent with 47 wt.% PEI on virgin silica.

The other goal of this work was to determine the composition of the pyrolysis liquid, identify



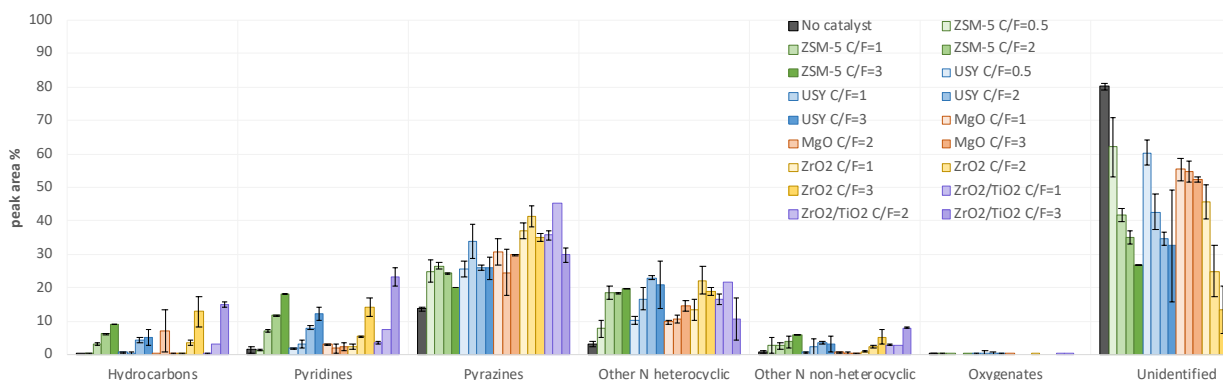
**Figure 3.** Composition of the oil from the pyrolysis of spent Si-PEI at different temperatures, as determined by qualitative GC-MS analysis.



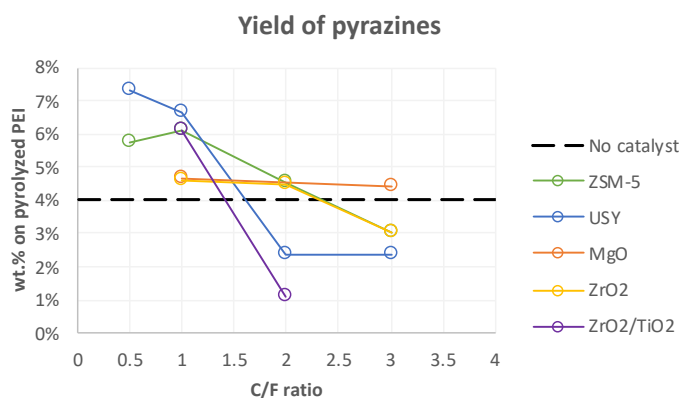
**Figure 4.** Pyrazine yields from the non-catalytic pyrolysis of spent Si-PEI at 400-650 °C (dark oil phase).

compounds of commercial interest, and maximize their yield. **Figure 3** presents the composition of the dark phase of the pyrolysis oils, as determined by qualitative GC-MS analysis. The light oil phase was also analyzed and was found to contain very similar chemical groups. For brevity, our analysis from now on focuses only on the dark oil phase. The majority of the chromatogram peaks could not be identified, which indicated the complexity of the pyrolysis oils that led to the poor separation of their compounds by the chromatographic column. Besides the unidentified peaks, the pyrazines were the most abundant compounds. Pyrazines are valuable chemicals that are used as food flavorings, fragrances, pharmaceuticals, insecticides or pheromones, and platform chemicals in organic synthesis and in the synthesis of novel polymers [9]. Other compounds, albeit in lower concentrations, were also identified, such as pyridines, hydrocarbons, other N-containing aromatic molecules, amines, and oxygenates. The pyrolysis temperature did not significantly affect the composition of the pyrolysis oils. The yield of the pyrazines was determined using a newly developed quantitative GC-MS method. The dark oil phase contained the majority of the pyrazines produced. The yields of pyrazines from the dark phase of the pyrolysis oils produced at different pyrolysis temperatures are presented in **Figure 4**. Pyrolysis at 400 °C yielded the lowest amount of pyrazines due to the incomplete pyrolysis of the PEI polymer. Increasing the pyrolysis temperature yielded up to 4.9 wt.% Pyrolysis at 500 °C or higher yielded about 6 wt.% pyrazines on the basis of the pyrolyzed PEI polymer.

To maximize the yield of pyrazines, the catalysts presented in **Table 2** were screened for the catalytic upgrading of the PEI pyrolysis vapors at 600 °C. In all cases, the catalysts resulted in increased gas yields due to the catalytic cracking of the PEI vapors and reduced pyrolysis oil yields (not presented for brevity). The dark oil phase yield decreased with all catalysts, while the yield of the light phase was affected less. However, the light oil phase from the catalytic pyrolysis runs was enriched in



**Figure 5.** Composition of the dark oil phase from the catalytic pyrolysis of spent Si-PEI at 600 °C with different catalysts and C/F ratios.



**Figure 6.** Yield of pyrazines from the catalytic pyrolysis of spent Si-PEI at 600 °C with different catalysts as a function of the C/F ratio.

water and contained fewer organics. The composition of the dark phase of the catalytic pyrolysis oils, as determined by qualitative GC-MS analysis, is presented in **Figure 5**. The catalysts significantly reduced the peak area % of the unidentified peaks and increased the concentration of the pyrazines in the pyrolysis oils. The concentration of other compound groups, such as hydrocarbons, pyridines, and other N-heterocyclics, also increased. **Figure 6** presents the pyrazine yields from the catalytic pyrolysis of the spent Si-PEI, as determined by quantitative GC-MS analysis. The highest pyrazine yields were obtained with the USY catalyst at C/F ratios 0.5 and 1. Higher C/F ratios led to more extensive cracking of the PEI vapors and reduced the pyrazine yield. The yield of pyrazines from the dark oil phase obtained with the USY catalyst at C/F=0.5-1 was about 7 wt.%, significantly higher than the yield of the pyrazines from the dark oil phase obtained from the non-catalytic pyrolysis at the same temperature.

Based on the results presented, it can be concluded that silica with high pore volume can be recovered from the pyrolysis of spent Si-PEI at 500 °C or higher. The recovered silica can be reused to produce fresh CO<sub>2</sub> adsorbents with high adsorption capacities. Pyrazines were obtained in the pyrolysis oil with a yield of up to 4.9 wt.%. Using a Y zeolite-based catalyst to upgrade the PEI pyrolysis vapors, the yield of pyrazines increased to 7 wt.%.

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