Simultaneous CO_2 capture and reactive nitrogen removal with a continuous-flow one-step supercritical water reactor

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ABSTRACT

- Carbon dioxide and reactive nitrogen emission from nitrogen-containing wastes are part of the global environmental issues.
- An advanced supercritical water oxidation (SCWO) process has been developed to simultaneously reduce the discharge of carbon dioxide and reactive nitrogen during the treatment of nitrogen-containing wastewater.
- By introducing $Ca(NO_3)_2$ to the reactor inlet and $Ca(OH)_2$ to the reactor outlet, 94% of the carbon and 95% of the reactive nitrogen in acrylonitrile (C_3H_3N) were simultaneously converted to solid $CaCO_3$ and innocuous nitrogen gas at 250 bar and 420 °C.
- In situ formed $CaCO_3$ in the reactor acted as a catalyst for the decomposition of acrylonitrile.
- The obtained $CaCO_3$ with average particle size of 1.72 µm can either be used for industrial applications or reconverted to $Ca(NO_3)_2$, which can be recycled to the reactor, and carbon dioxide, which can be injected into deep geological formations.
- This novel method provides an inherently cleaner SCWO process which offers an attractive solution for the capture of carbon dioxide and reduction of total nitrogen (TN) from nitrogen-containing wastewater, as well as the removal of total organic carbon (TOC).

Scalable continuous-flow one-step process for simultaneous CO_2 capture and reactive nitrogen removal

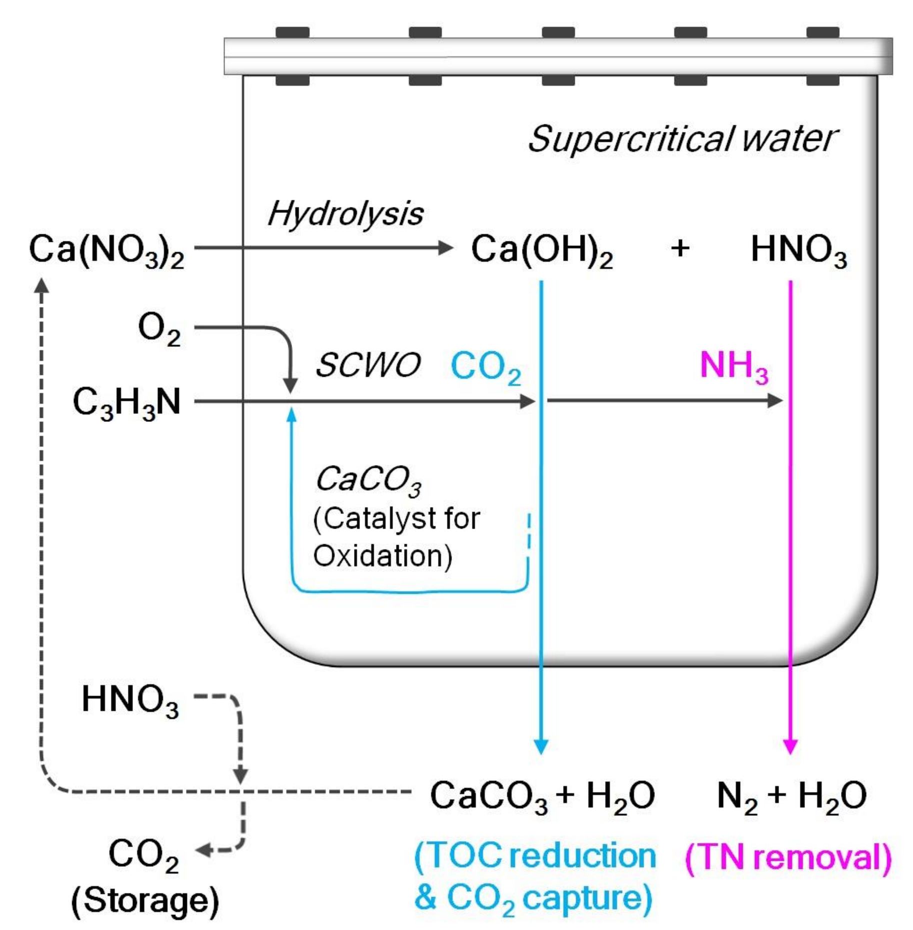

Fig. 1. Reaction pathways during the oxidation of acrylonitrile in supercritical water in the presence of $Ca(NO_3)_2$.

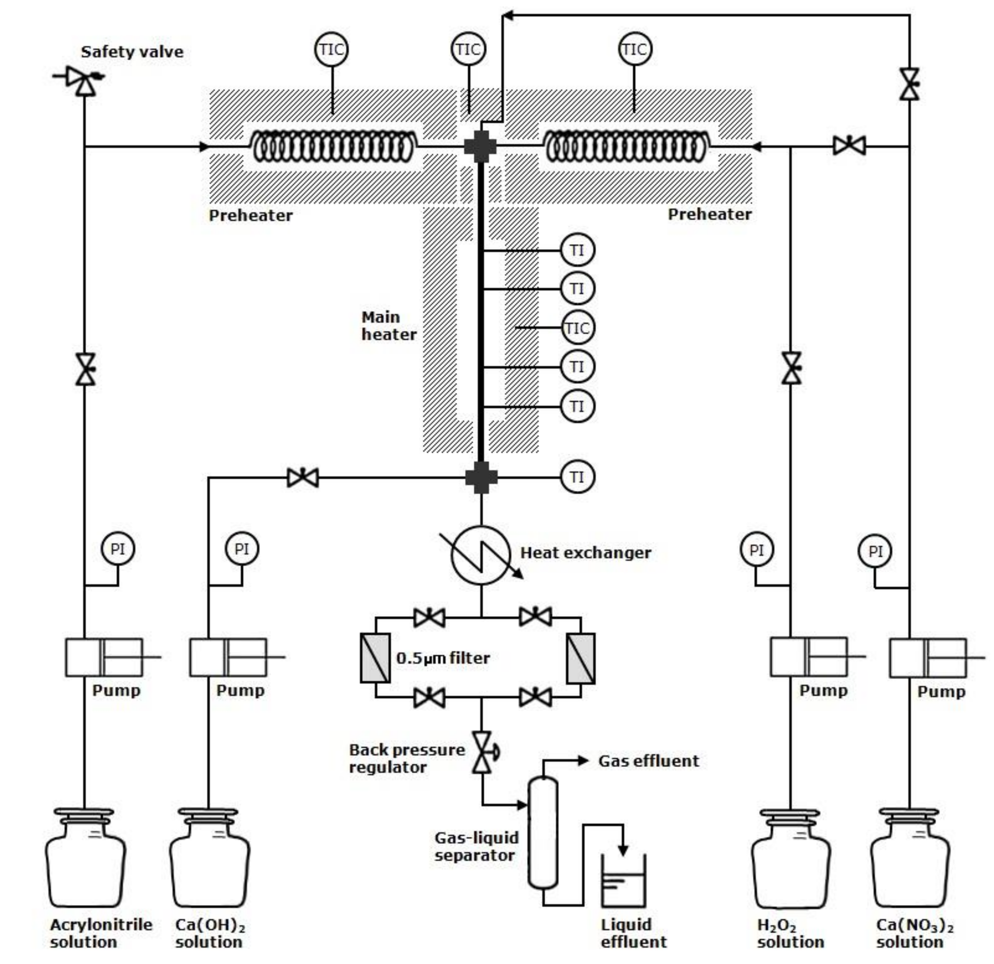

Fig. 2. Schematic of experimental apparatus for the simultaneous reduction of CO_2 and reactive nitrogen during the SCWO of acrylonitrile.

REMOVAL OF REACTIVE NITROGEN

- The conventional SCWO of acrylonitrile in the absence of $Ca(NO_3)_2$ resulted in the removal of 94% of the TOC under the following conditions: 250 bar, 481 °C and 10 sec reaction time with a 1.5:1 stoichiometric ratio of oxygen to acrylonitrile (Fig. 3A).
- With respect to TN, only 14% removal was achieved under the same conditions due to the fact that the ammonium generated from acrylonitrile is relatively unreactive during the conventional SCWO.
- On the other hand, the direct introduction of $Ca(NO_3)_2$ to the reactor resulted in the removal of 95% of the TOC and 85% of the TN even at a lower reaction temperature of 423 °C with all other variables held constant (Fig. 3B).
- TOC in the liquid effluent was dramatically reduced due to catalytic effect of $CaCO_3$.

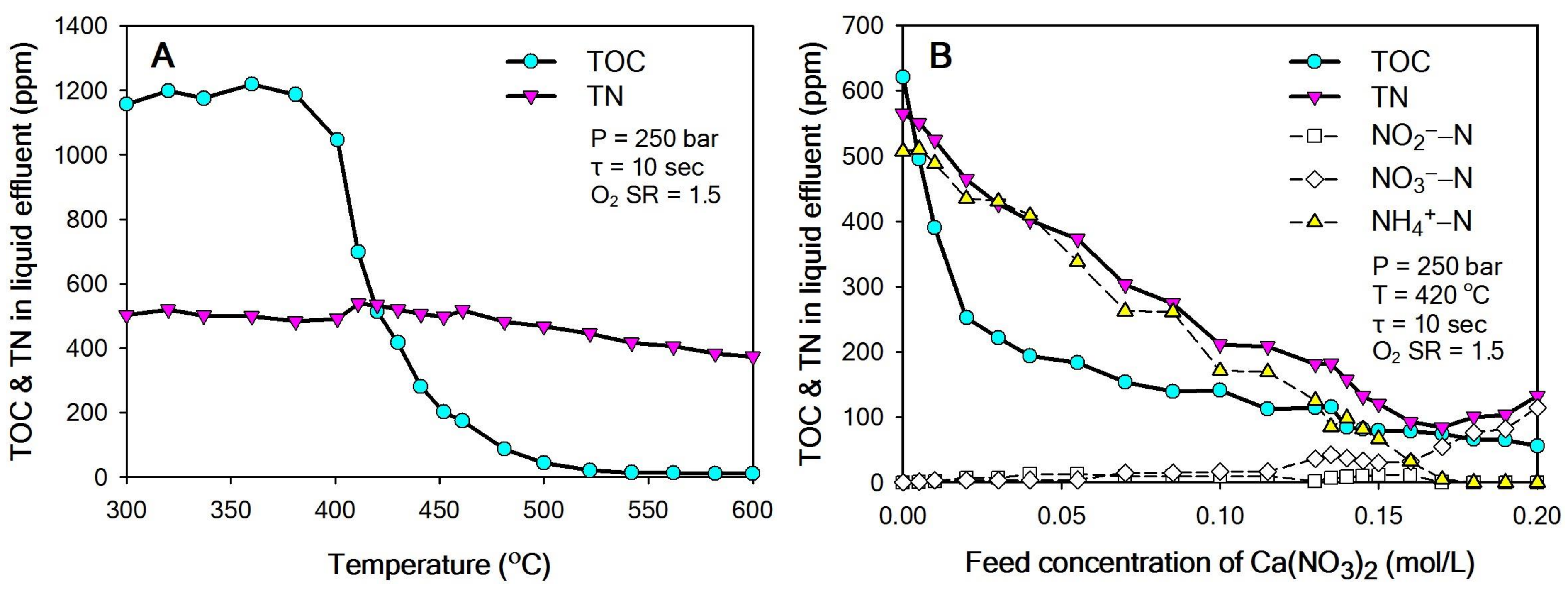

Fig. 3. (A) Effects of reaction temperature on TOC and TN in the liquid effluent from the continuous SCWO of acrylonitrile. (B) Effects of $Ca(NO_3)_2$ feed concentration on TOC and TN in the liquid effluent from the continuous SCWO of acrylonitrile at 420 °C.

CO_2 CAPTURE

- It is suggested that $Ca(NO_3)_2$ is hydrolyzed to $Ca(OH)_2$, followed by reaction of $Ca(OH)_2$ with carbon dioxide generated by the SCWO of acrylonitrile to produce $CaCO_3$.
- This in situ formed $CaCO_3$ acts as an effective oxidation catalyst for the decomposition of acrylonitrile in supercritical water.
- Fig. 4A demonstrates that the particles collected from the reactor effluent were $CaCO_3$, as confirmed by X-ray diffraction analysis.
- The number-weighted average particle size of the obtained $CaCO_3$ was 1.72 µm.
- Nitrate from $Ca(NO_3)_2$ reacted with ammonium, generated by the SCWO of acrylonitrile to produce benign nitrogen gas.

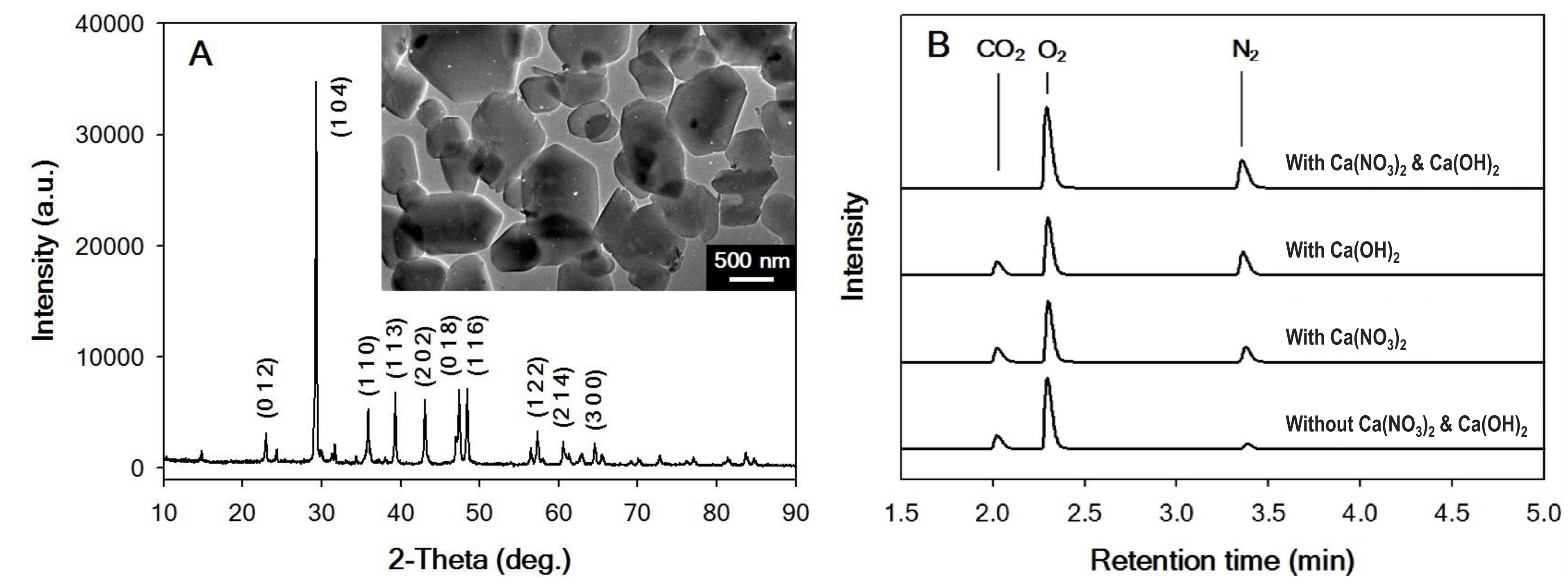

Fig. 4. (A) X–ray diffraction pattern and transmission electron micrograph of particles obtained during the continuous SCWO of acrylonitrile in the presence of $Ca(NO_3)_2$. (B) Gas chromatograms of gas effluents from the continuous SCWO of acrylonitrile in the presence of $Ca(NO_3)_2$ and $Ca(OH)_2$.

CONCLUSIONS

- 94% carbon of acrylonitrile feed was captured as $CaCO_3$ by introducing $Ca(NO_3)_2$ to the reactor inlet and $Ca(OH)_2$ to the reactor outlet.
- Simultaneously, 85% reactive nitrogen was reduced by the reaction of nitrate from $Ca(NO_3)_2$ with ammonium from acrylonitrile at 420 °C.
- The developed novel process provides a flexible platform for wastewater treatment which simultaneously reduces the discharge of TOC, reactive nitrogen, and CO_2.

ACKNOWLEDGMENTS

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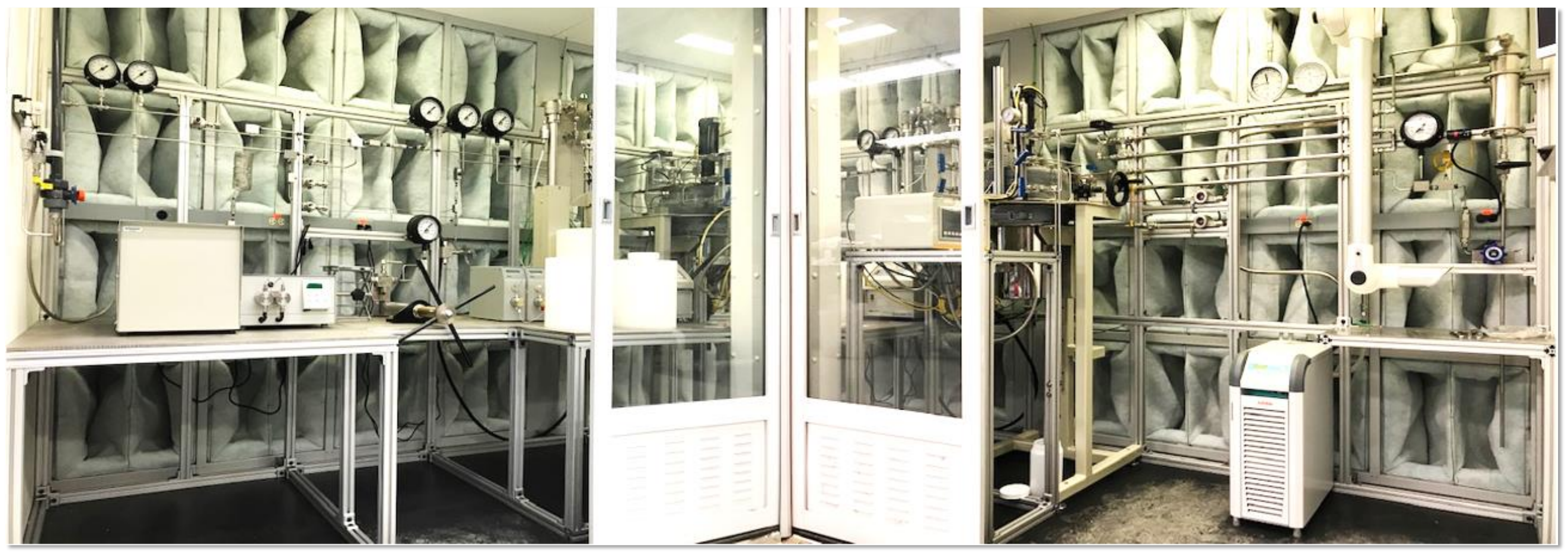

Fig. 5. Multi-purpose batch-type supercritical fluids processing system at ANL MERF