

Effects of zero-valent iron nanoparticles on lactate-based chain elongation

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Abstract

HIGHLIGHTS:

- nZVI affected chemical and biological processes.
- n-caproate was formed only in the presence of nZVI.
- nZVI could potentially be replaced with (bio)electrochemistry.

BACKGROUND: Production of biochemicals from renewables is of outmost importance to reduce anthropogenic impact on the environment. A mixture of carboxylates (acetate [C2], propionate [C3], n-butyrate [nC4], n-valerate [nC5], n-caproate [nC6]) can be produced through chain elongation of substrates such as lactate and steering to MCC is desired since these are easily separated and used in the chemical and food industries³. Chain elongation can be steered with different operational conditions such as pH, HRT, electron donor-to-acceptor ratio and hydrogen partial pressure³. In this study, zero-valent iron nanoparticles (nZVI) were tested as catalyst to steer product formation in chain elongation. Dosing nZVI could stimulate several enzymes involved in lactate metabolism such as lactate enantiomers interconversion, lactate oxidation, pyruvate oxidative decarboxylation, hydrogen formation and energy conservation. Carbon dioxide (CO₂) recovery via acetate or alcohol formation could also be promoted. These effects would be reflected in altered conversion rates and product spectra.

RESULTS & DISCUSSION: Addition of nZVI to a mixture of lactate monomers and oligomers (polyesters) resulted in chemical hydrolysis of lactate oligomers by alkaline de-esterification (Figure 23). Under fermentative conditions, lactate and acetate were elongated to nC4-nC6 carboxylates with hydrogen release to the headspace. This

chain elongation phase was followed by a hydrogen/ CO_2 consuming phase for acetate formation. Lactate conversion rates were improved at $\leq 2 \text{ g nZVI}\cdot\text{L}^{-1}$ promoting n-caproate production. n-caproate was not produced in the control experiment without nZVI but reached $4.3\pm 0.3 \text{ g}\cdot\text{L}^{-1}$ at $1 \text{ g nZVI}\cdot\text{L}^{-1}$. Propionate formation became relevant when $\geq 3.5 \text{ g nZVI}\cdot\text{L}^{-1}$ were added. CO_2 recovery was not clearly increased with nZVI (Figure 24). Both lactate enantiomers (D-lactate and L-lactate) were racemized during chain elongation and converted into even-chain carboxylates at different rates.

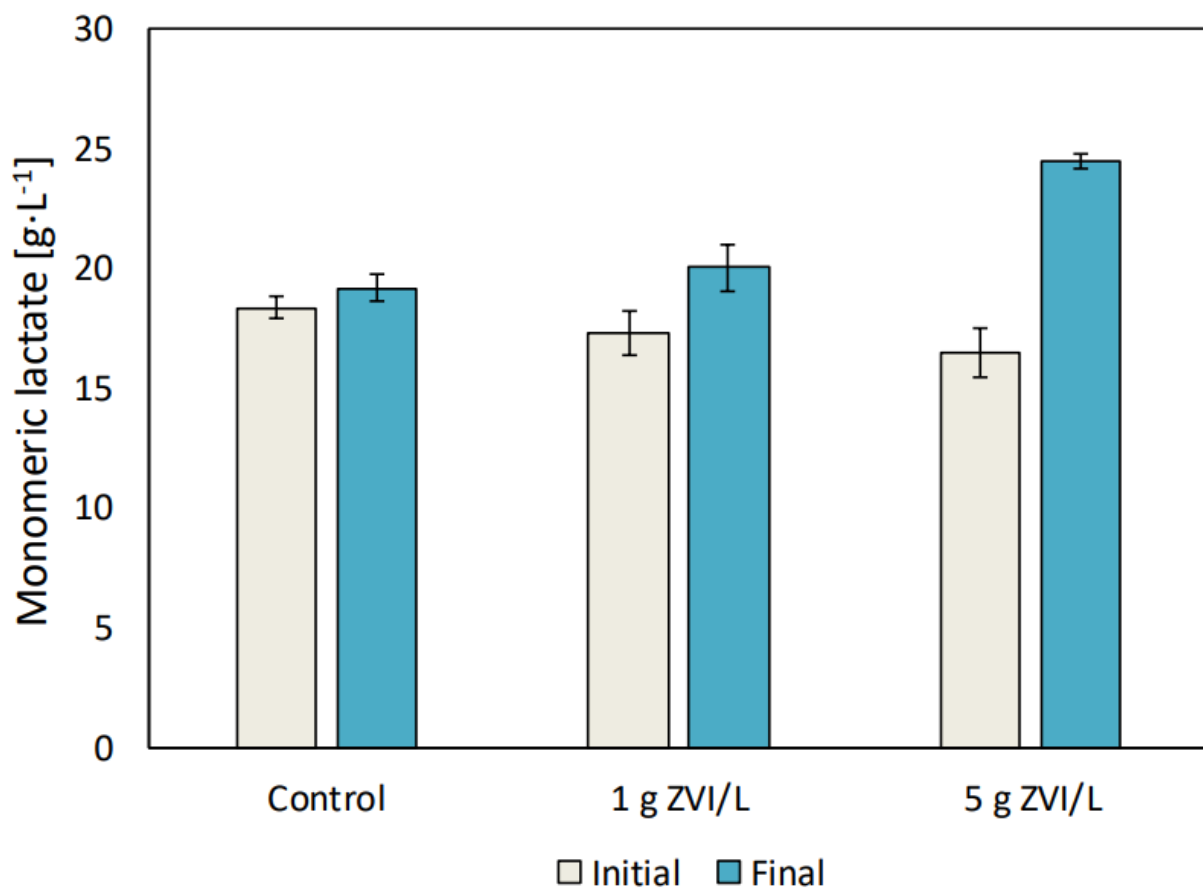


Figure 23. Increase in lactate monomers due to lactate oligomers hydrolysis.

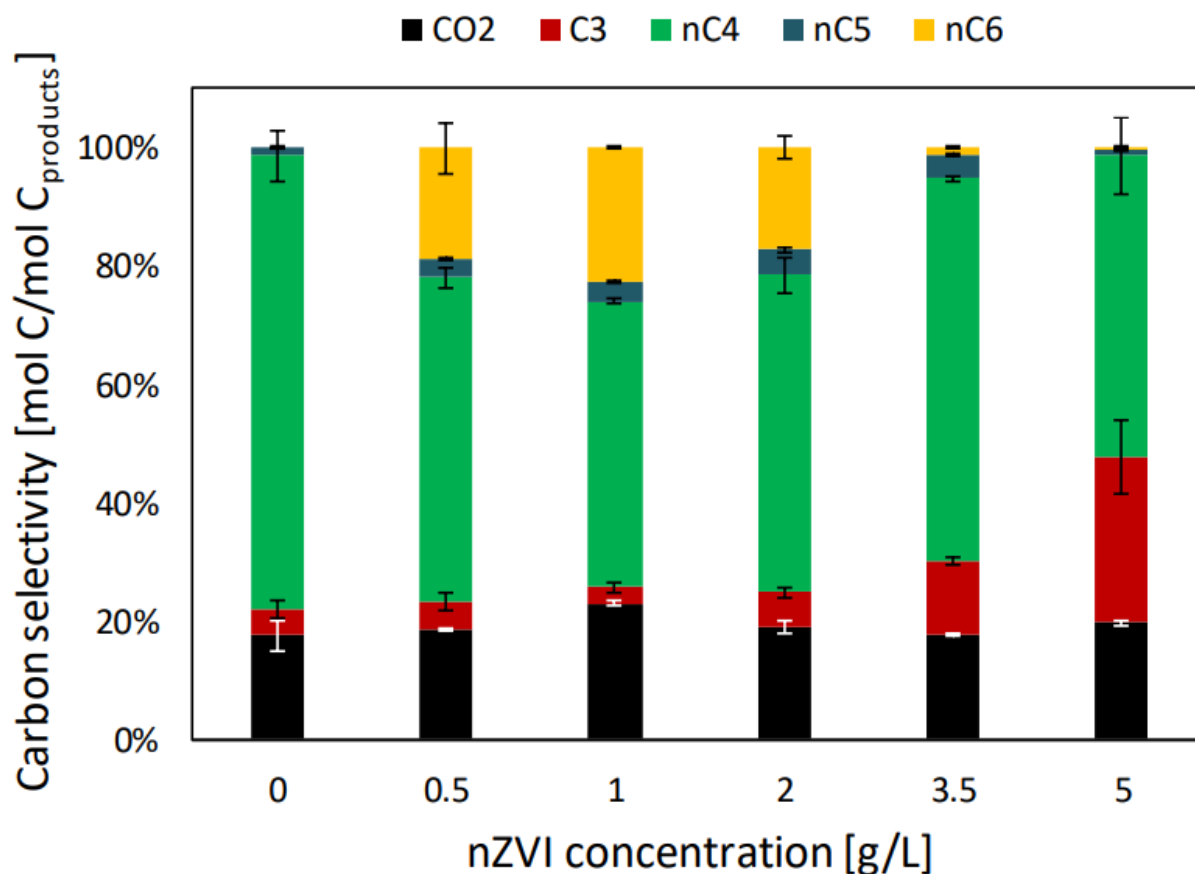


Figure 24. Effect of nZVI concentration on product spectrum.

CONCLUSIONS: nZVI enhanced hydrolysis of lactate oligomers increasing substrate availability. Lactate-based chain elongation products and rates were affected in a dose-dependent manner by nZVI with no observed microbial activity inhibition. The effects of nZVI could be on the oxidation-reduction conditions, electron donor and pH changes. Lactate enantiomeric proportions were observed to be determined by the type of metabolism (chain elongation vs acrylate pathway) and, therefore, feeding D-lactate in continuous reactors would not necessarily translate into higher chain elongation rates. The different effects of nZVI may be improved in different system configurations and partially replaced with (bio)electrochemical systems.