Removing Chlorine from Plastic using Thermochemical Pretreatment

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Mainstream Engineering Corporation

- Small business incorporated in 1986
- 100+ employees
- Mechanical, chemical, electrical, materials and aerospace engineers
- 100,000 ft^2 facility in Rockledge, FL
- Laboratories: electric power, electronics, materials, nanotube, physical and analytical chemistry, thermal, fuels, internal combustion engine
- Manufacturing: 3- and 5- axis CNC and manual mills, CNC and manual lathes, grinders, sheet metal, plastic injection molding, welding and painting

1 - ENGINEERING OFFICES
2 - RESEARCH & DEVELOPMENT
3 - RESEARCH & DEVELOPMENT
4 - PRODUCTION
5 - PRODUCT DEVELOPMENT
5a - MAINSTREAM EBEAM
6 - CONTROLLED-ATMOSPHERE BRAZING FACILITY
7 - SHEET METAL FABRICATION
8 - ROTOMOLD PRODUCTION

Capabilities

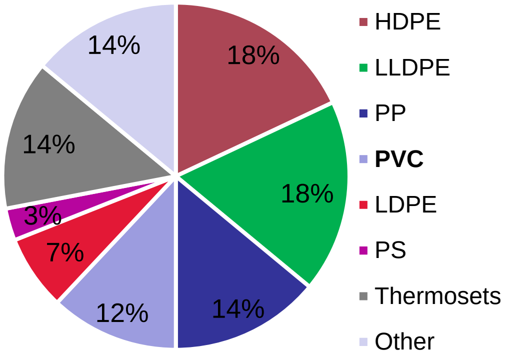
- **Basic and Applied R&D**
- **Transition from R&D to Production**
- **Manufacture Advanced Products**

Mission Statement

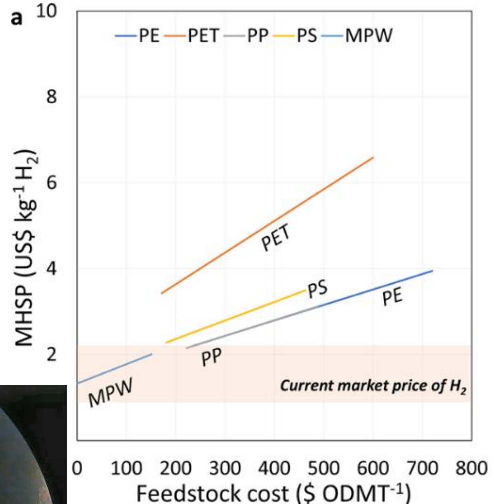
To research and develop emerging technologies.
To engineer these technologies into superior quality, military and private sector products that provide a technological advantage.

Problem

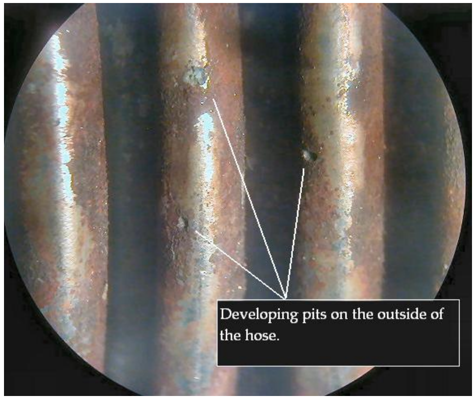
- **Gasification enables the production of clean hydrogen from renewable resources, mixed waste, and plastics**
  - Converts material into syngas at >700 °C
  - Controlled oxygen/steam
- **380 MT of low-cost mixed waste**
  - High-chlorine content feedstocks (e.g., PVC) make up over 12% of all U.S. plastics
- **Gasification of chlorine feedstocks leads to many gasification issues**
  - High-temperature corrosion >450 °C
  - Forms volatile metal chlorides
  - Promote degradation of heavy metals into chlorides (e.g., dioxins) or acidic gases
  - Deactivate catalysts
- **Even with syngas cleaning -> corrosion and increased maintenance costs**



Plastic blend in waste



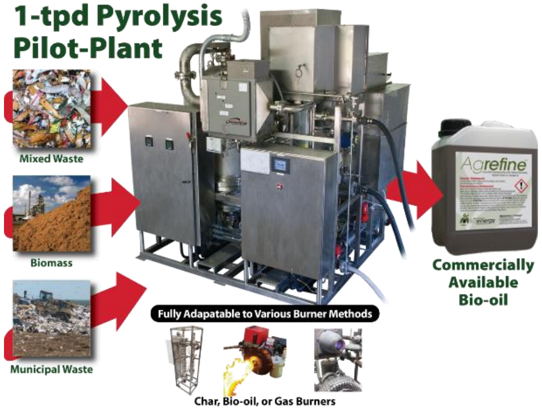
Price of plastic wastes[1]



Example of chlorine corrosion on heat exchanger pipes[2]

Potential Solutions

- **Fate and form of chlorine dependent on thermochemical process**
  - Low-temperature carbonization (<300 °C) HCl released, can stay in solid
  - Medium-temperature pyrolysis (300–600 °C), Cl species released to oil and gas
  - High-temperature gasification (>700 °C), Cl species released as gas
- **Mainstream has three processes in these lower temperature regimes**



Hydrothermal Processing

- Wet wastes
- 150–350 °C
- Water medium
- Aqueous

Torrefaction

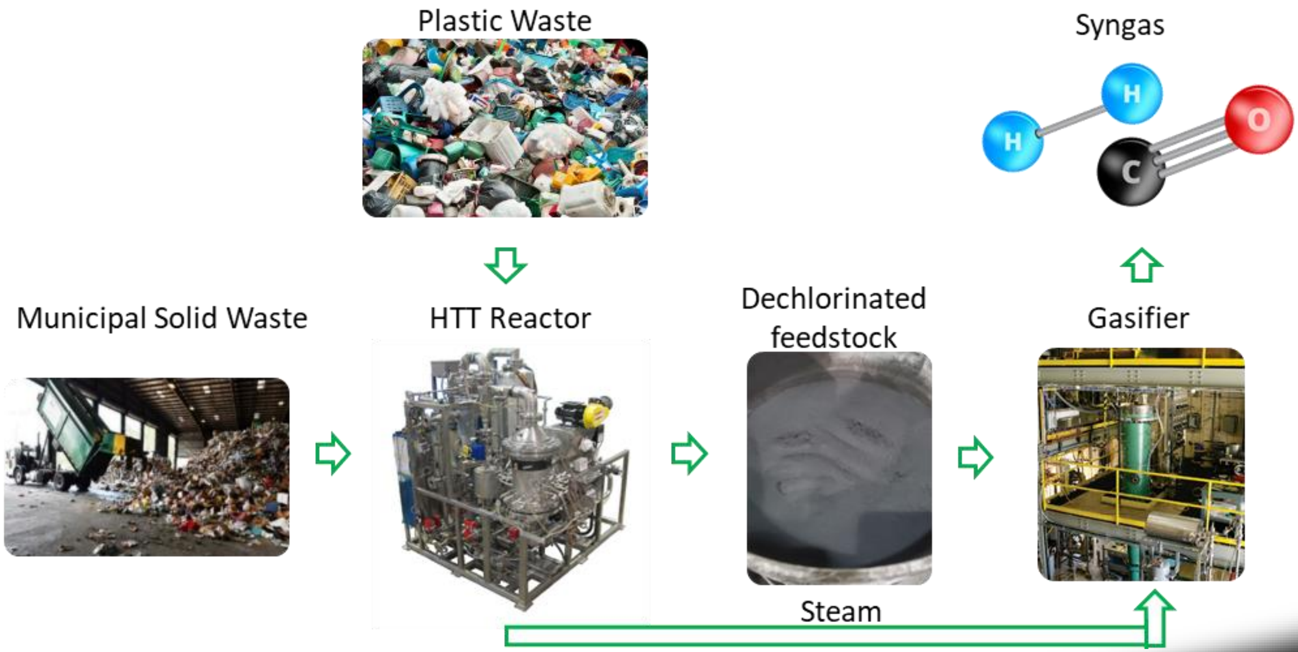
- Dry wastes
- 250–350 °C
- Inert gas
- Volatile gas, solid

Pyrolysis

- Dry wastes
- 400–600 °C
- Inert gas
- Gas, oil, solid

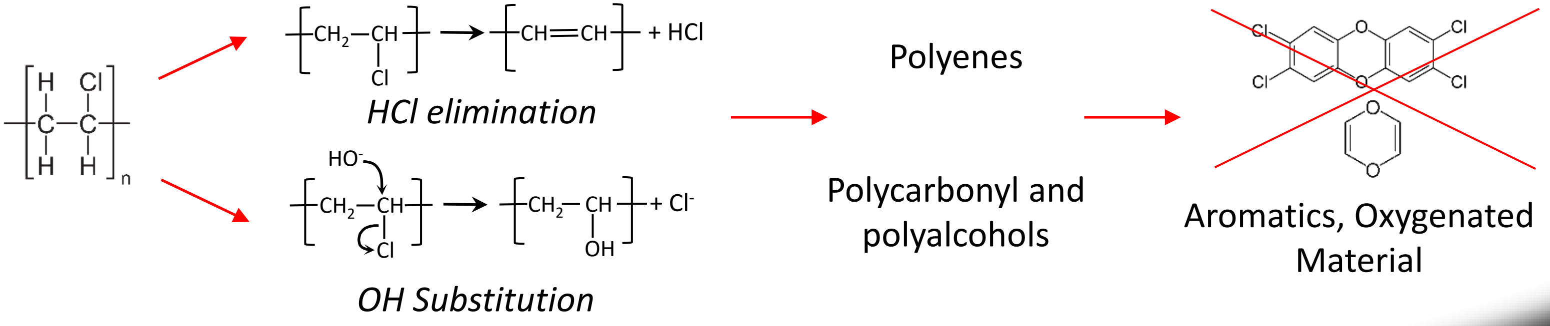
Mainstream's HTT Approach

- **Hydrothermal Treatment (HTT) offers the most benefits**
  - Chlorine ends up in aqueous phase as chloride, and not the primary gasification feed (extends gasifier lifespan, simplifies post-processing)
  - Improves pulverization characteristics
  - Combination of pyrolytic and hydrothermal reactions
    - More pathways, i.e. hydroxyl groups enhance reaction by –OH substitution of –Cl
    - Need additional understanding of mechanisms, reaction enhancers, optimization and scalability



Hydrothermal Breakdown of PVC/Plastic

- **Medium-temperature** (200 – 300 °C)
  - HCl released before further degradation
  - Enhanced by presence of catalyst/reactants (HCl, bases, solvents)
    - Mixed results in literature
    - Target hydroxide substitution and HCl autocatalysis
- **High-temperature** (>300 °C)
  - May produce chloroalkanes, chlorinated dioxins
  - Consumes energy from plastic, bad pre-treatment method



Target Objectives

Develop a thermochemical preprocessing technology to dechlorinate plastics for subsequent gasification

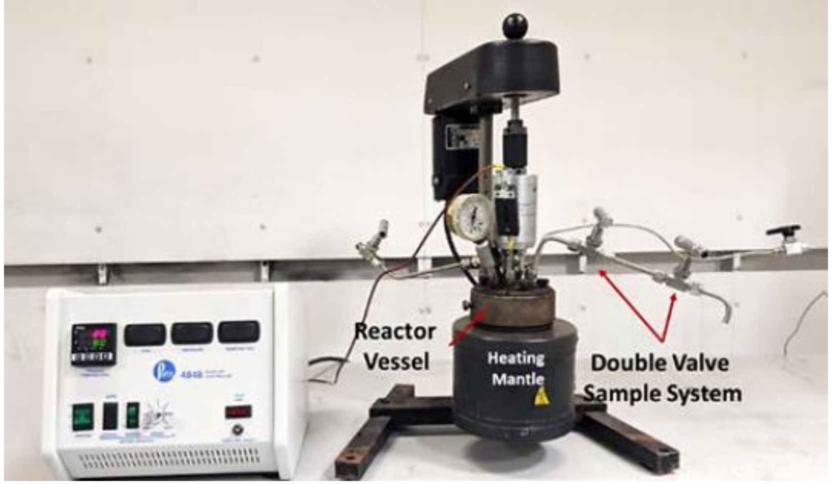
- Optimize chemistry with PVC, mixed plastics, and then MSW
- Develop the process and scale-up the technology

Target – Remove all of the chlorine, densify the product, and keep all of the energy

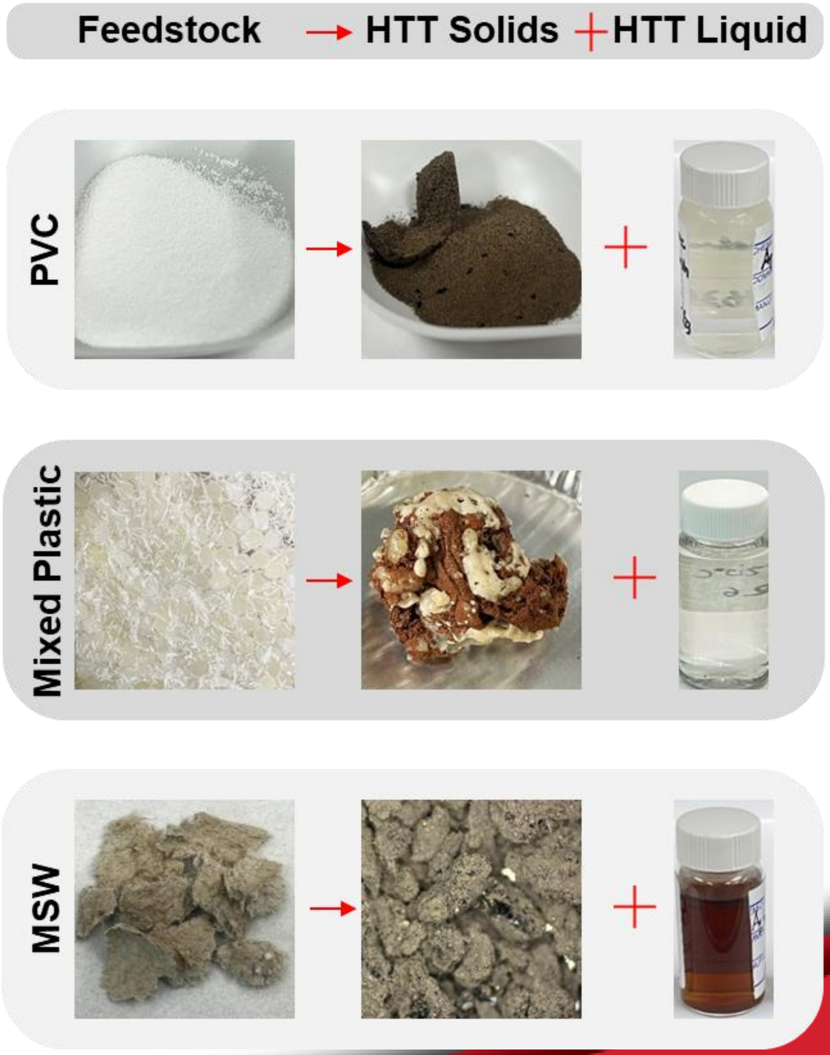
Objective	Result
Demonstrate >98% removal of chlorine from PVC, mixed plastic waste, and MSW	• Demonstrated >99.9% chlorine removal
Retain >95% of MSW after the HTT process	• Demonstrated retaining >90% of inlet energy content at 180% densification • Drastically reduces shipping and operating costs
Show an HTT processing cost of <$100/ton	• At scales >50 tons/day, operating costs <$100/ton
Demonstrate an integrated HTT-gasifier improves total economics (e.g., payback period, profit)	• Expected profit of $40/ton at 100 tons/day when MSW is dechlorinated and sold at an equivalent heating value of coal • Integrated waste heat increases expected profit to >$60/ton • Payback period is <3 years with 5-year amortized capital costs

HTT Chemistry Optimization

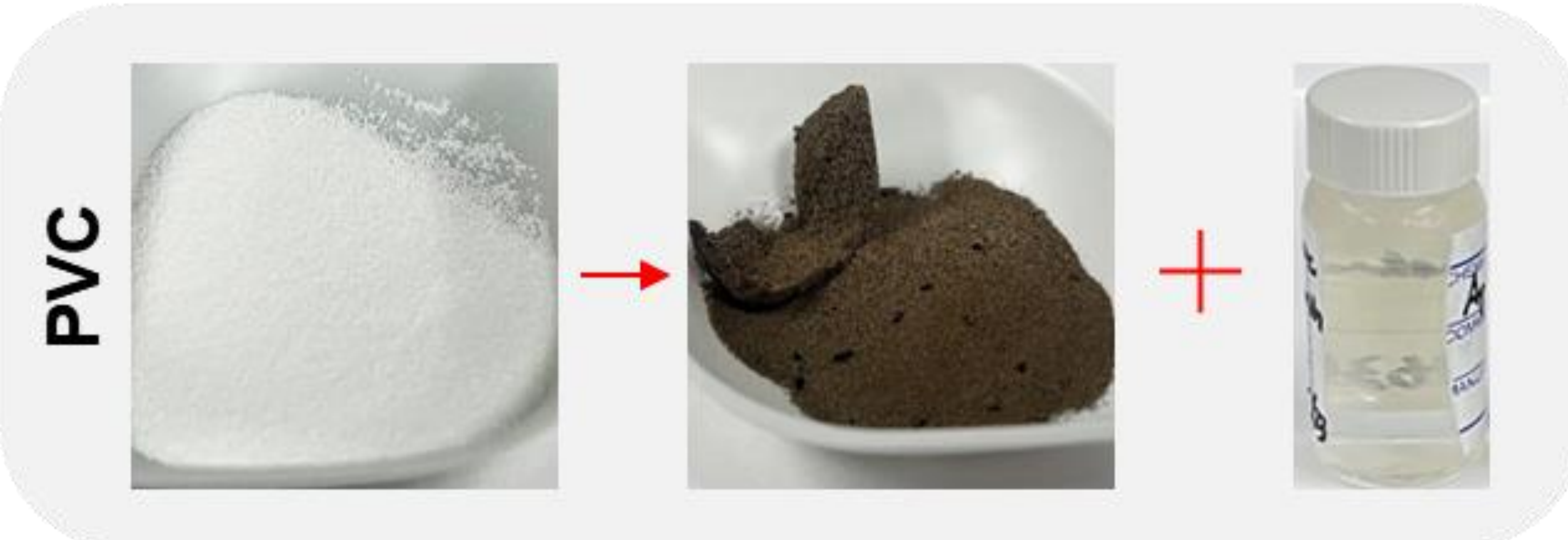
- **HTT of virgin and recycled materials**
- **Time resolved and product analysis**
  - Liquid – pH, Cl^- titration, TOC
  - Solid – Mass loss, FTIR, elemental analysis
- **Dechlorination efficiency metric based on [Cl^-]**
  - DE = Cl in solution / initial Cl in solid
- **Evaluate reaction enhancers**



Batch Parr reactor and double valve system

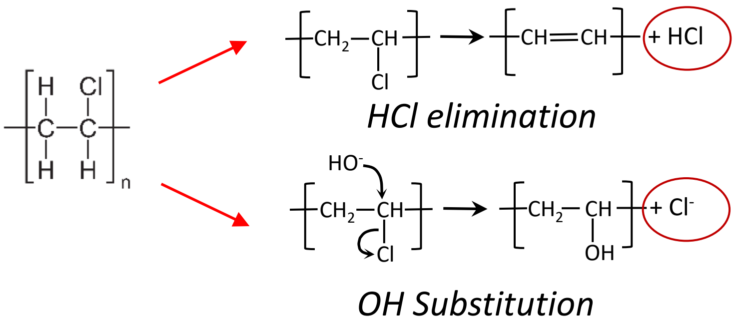


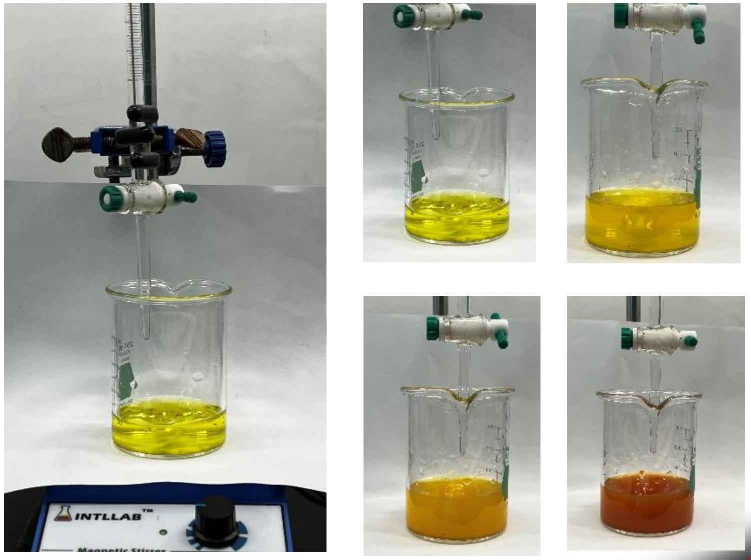
HTT of PVC



HTT of PVC Baseline (Autothermal)

- **Autothermal = Pure water**
- **PVC releases HCl at temperature**
  - pH of water ↓
- **Dechlorination efficiency measured by chlorine found in aqueous fraction**
  - Chloride titration (Mohr's method)
- **Increasing temperature increases dechlorination and carbonization**
  - Best result ~95% conversion (30 mins)
- **High initial PVC loading leads to high concentrations of acid (pH <1)**
  - Want high loading to decrease costs at scale
- **Acidic products are not ideal for scale-up, economics, general feasibility**

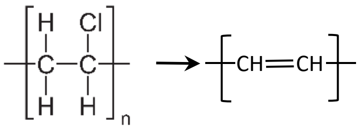


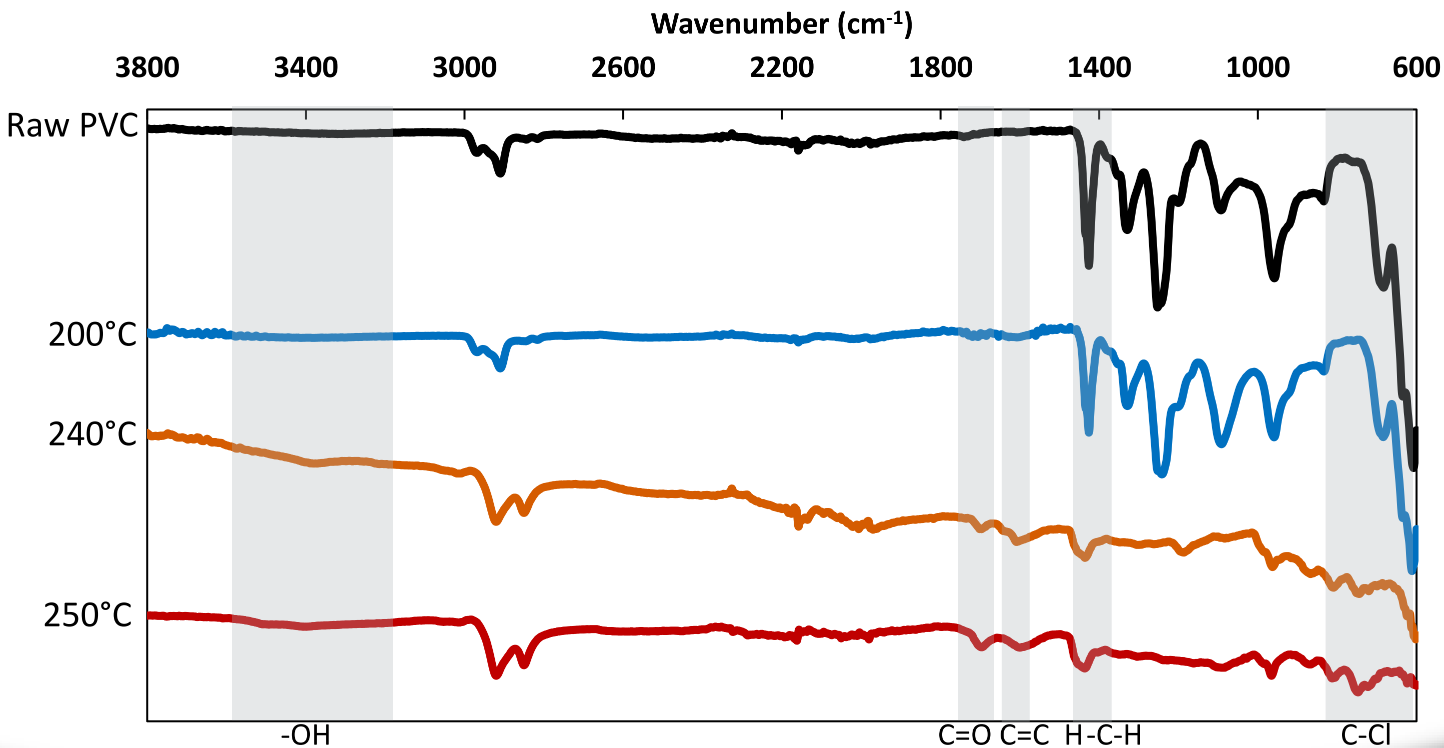


Chloride titration

Mechanism Analysis – FTIR of Solids

- **Hydrothermal carbonization produces hydrochar product**
  - Removes chlorine
  - Minimal OH substitution
  - C=C bonding (elimination)



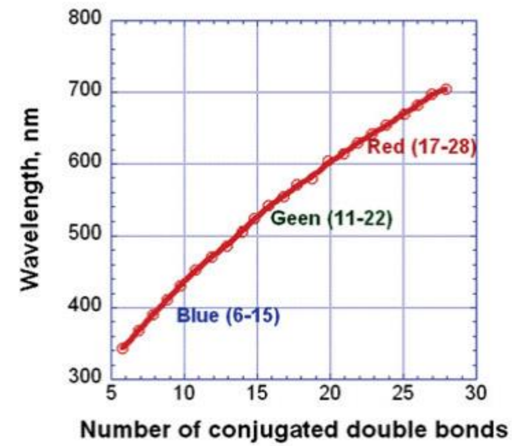


Virgin PVC

HTT Product

Mechanism Analysis – Solids Color

- **Polyene chain growth observed** (elimination)
- **Conjugated double bond chains absorb light frequencies based on length**
  - Short chains absorb blue light, looks yellow
  - Presence of longer chains will also absorb green, product looks red
  - More complete reaction looks dark
- **Spectrum from raw to carbonized** (%DE shown)



Raw PVC

2%

6%

15%

27%

Mixed DE

37%

49%

50%

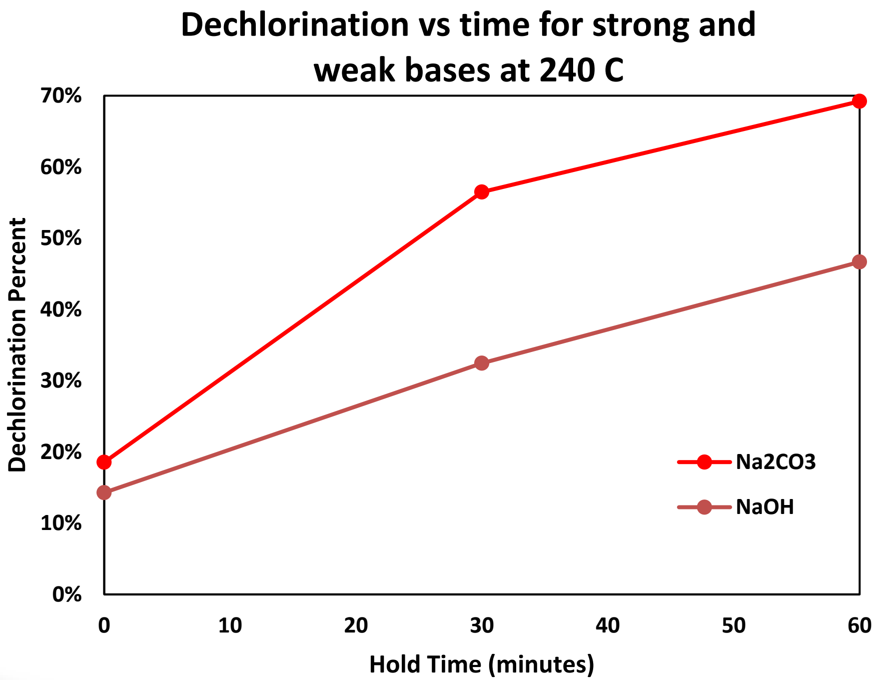
60%

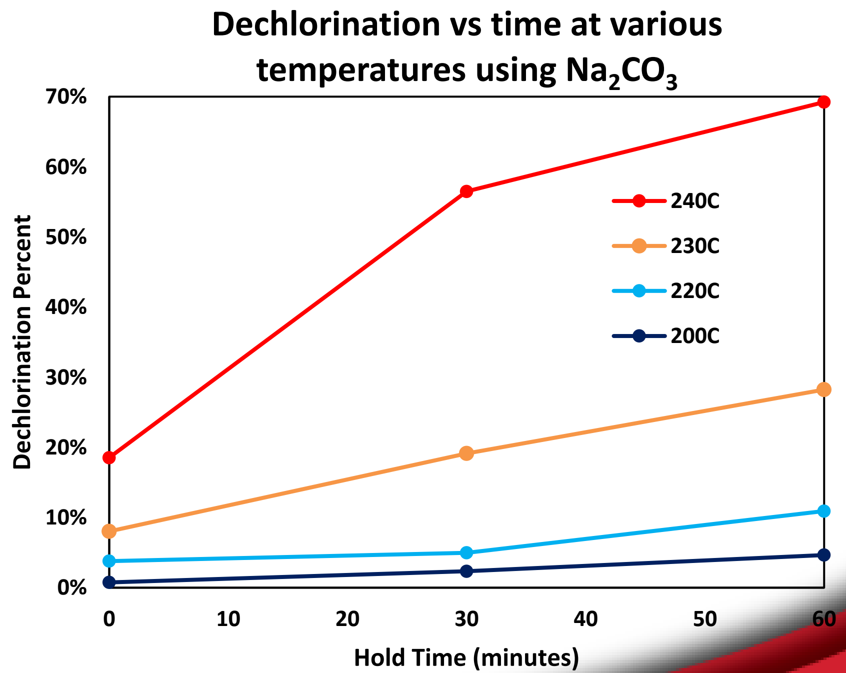
100%

Dechlorination Efficiency

HTT of PVC with Base Addition

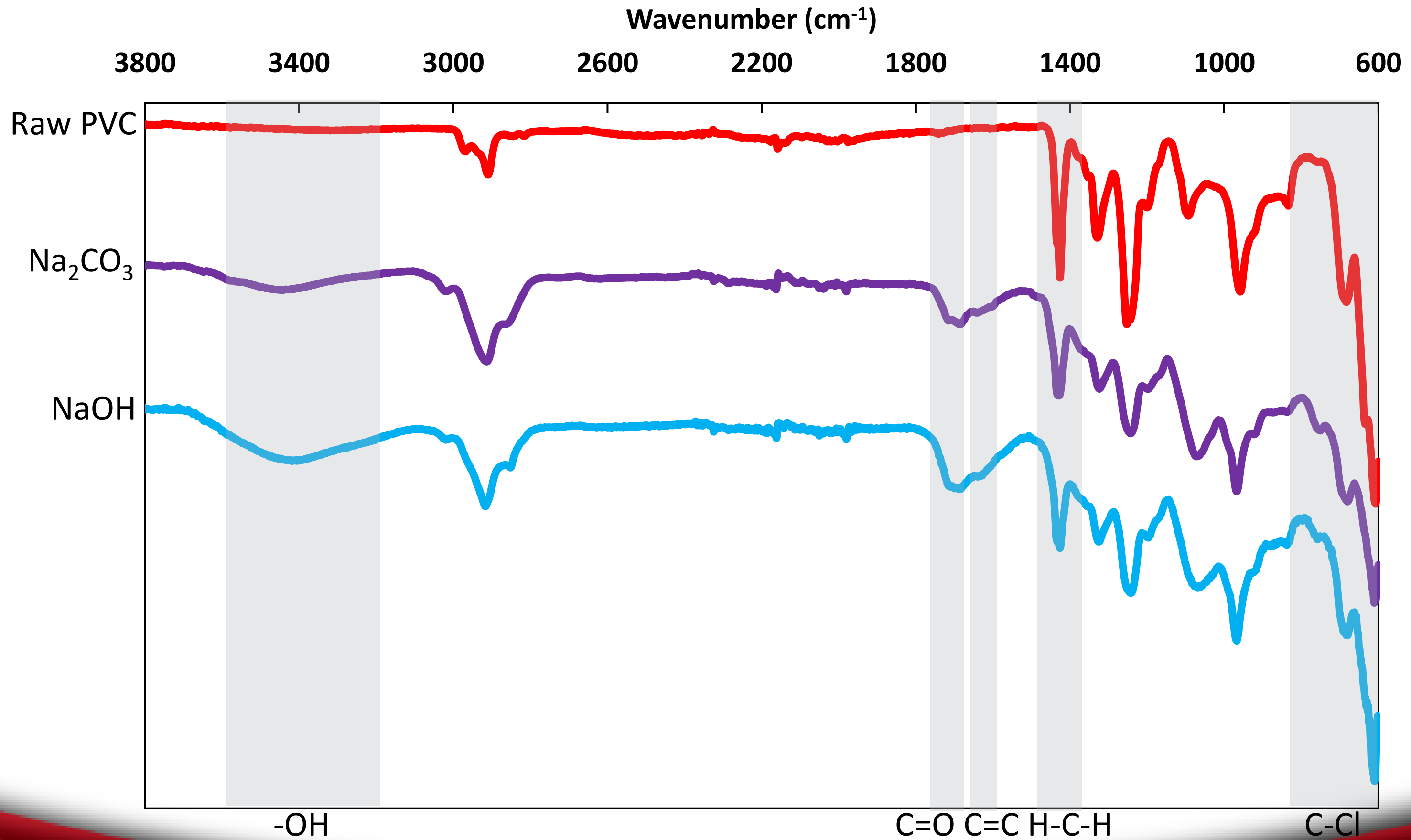
- **Base can act catalytically to increase reaction rate**
- **Longer times and higher temperatures increase conversion**
- **Weak base more effective than strong base**
  - Using stoichiometric concentration (to HCl), 0.16 M

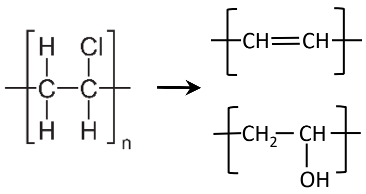




Mechanism Analysis – Solids with Base

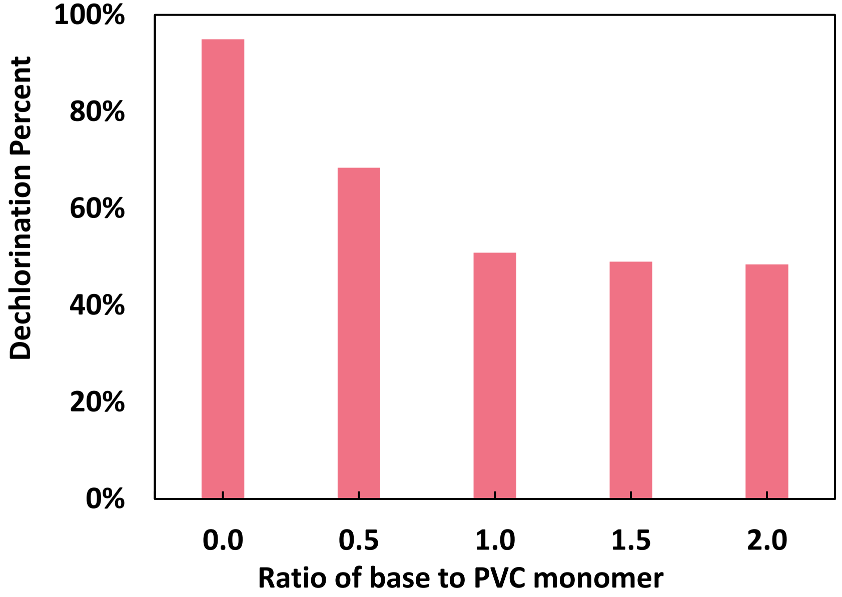
- **Peaks indicate alcohols, double bonds, and carbonyls were added to PVC**
  - Strong base produces strongest -OH peak
  - More OH substitution but less overall dechlorination than autothermal





HTT of PVC with Base – Concentration

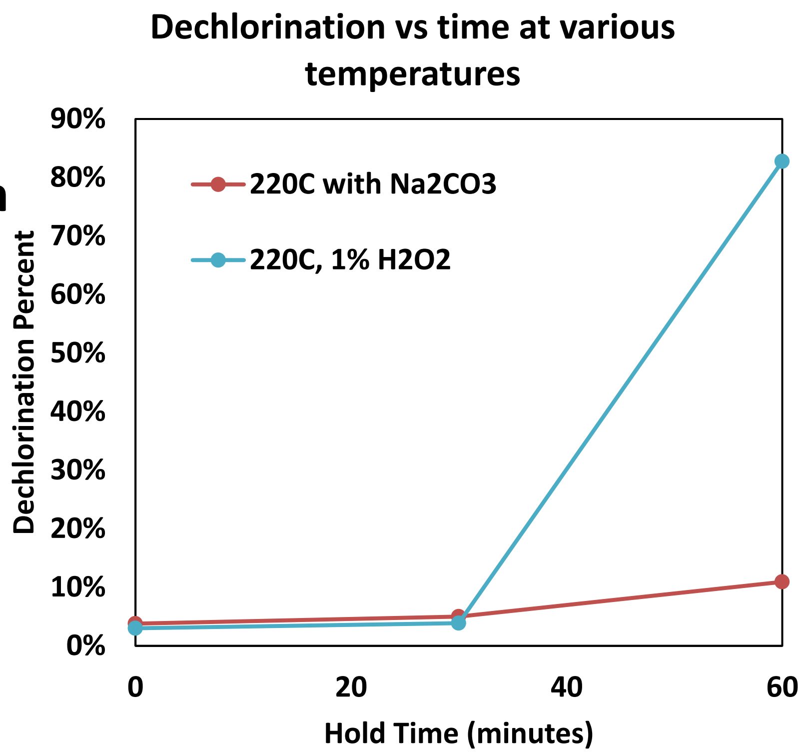
- **Increasing base, decreased conversion until excess**
  - OH^- mechanism slower
  - Base may hinder HCl autocatalysis
- **Base neutralized acid produced and prevented corrosion**
  - Best for scale-up, equipment material construction and lifetime
  - Removes downside of higher temp (faster corrosion)



- **Still want to speed reaction at reduced temperature**
  - Reduce heating, pressure, equipment/materials -> cost
  - Other reaction enhancers

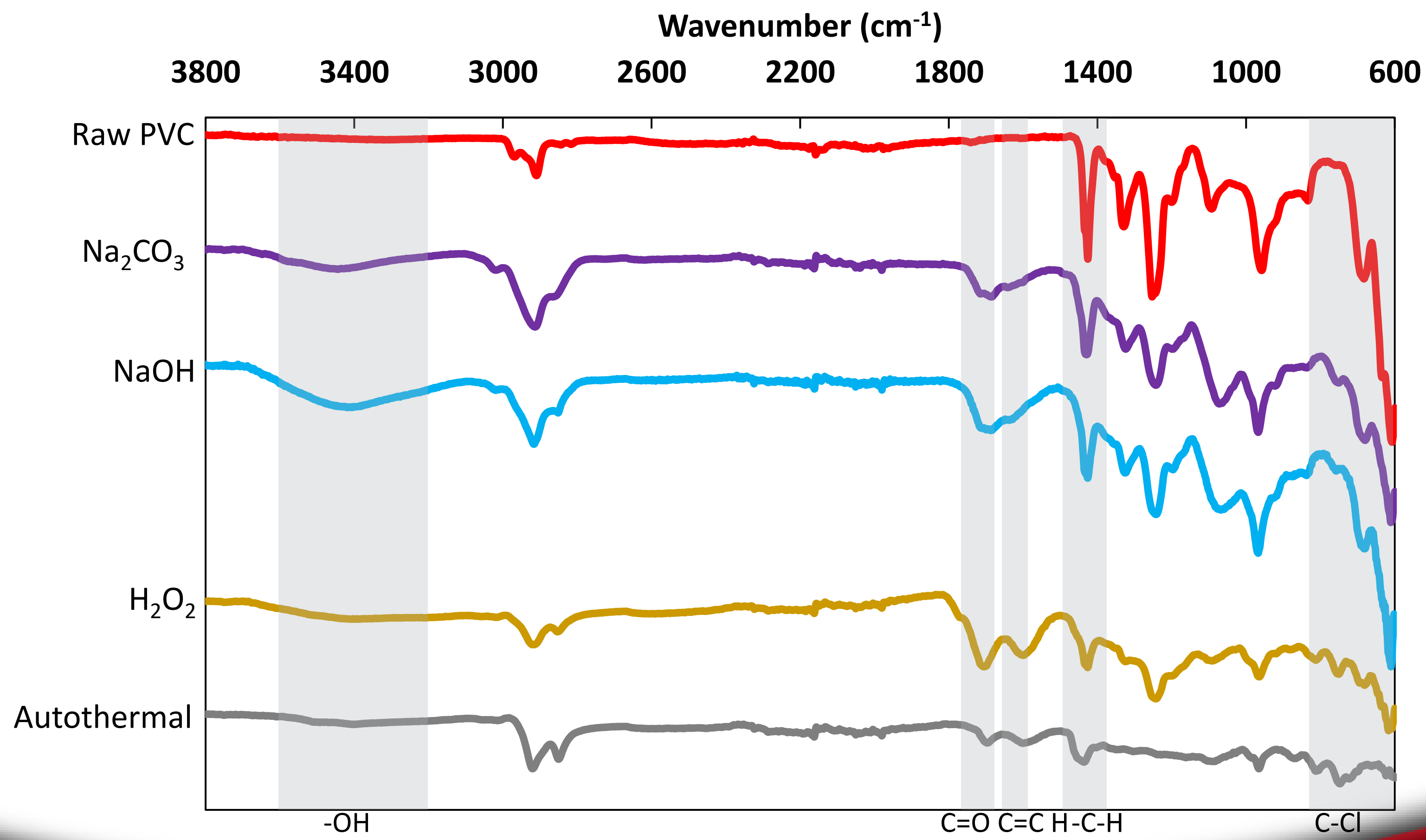
HTT of PVC with H_2O_2

- **Radicals and oxygen have shown positive effect on PVC dechlorination**
  - Peroxide source of both
- **Significantly improved dechlorination at low temperatures compared to basic conditions**
  - Effective at low concentrations (0.5%, 1%, and 3%)



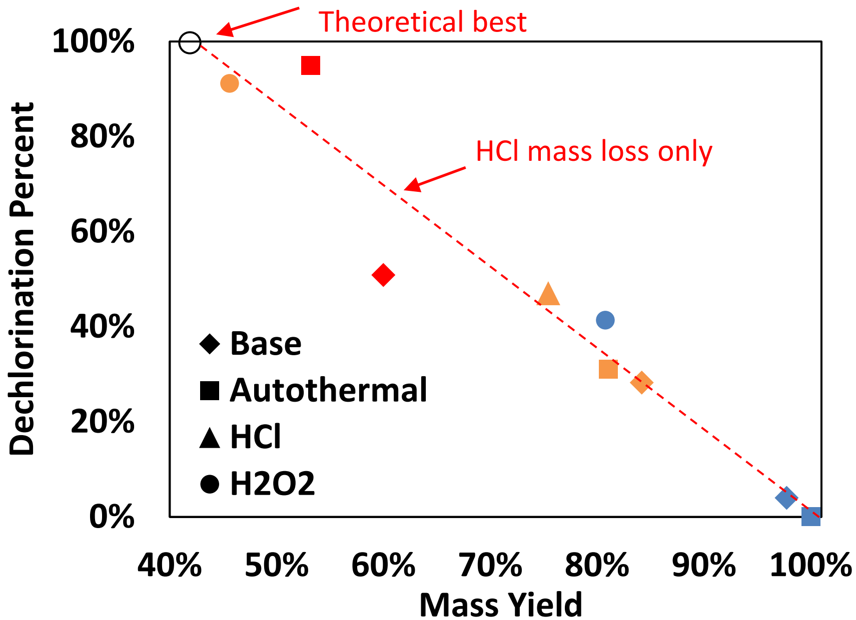
Elimination Mechanism Dominates

- H_2O_2 shows greatest carbonyl peak, oxidation of material
- Small C-Cl, large C=C → dechlorination by elimination



Best Reaction Conditions for PVC

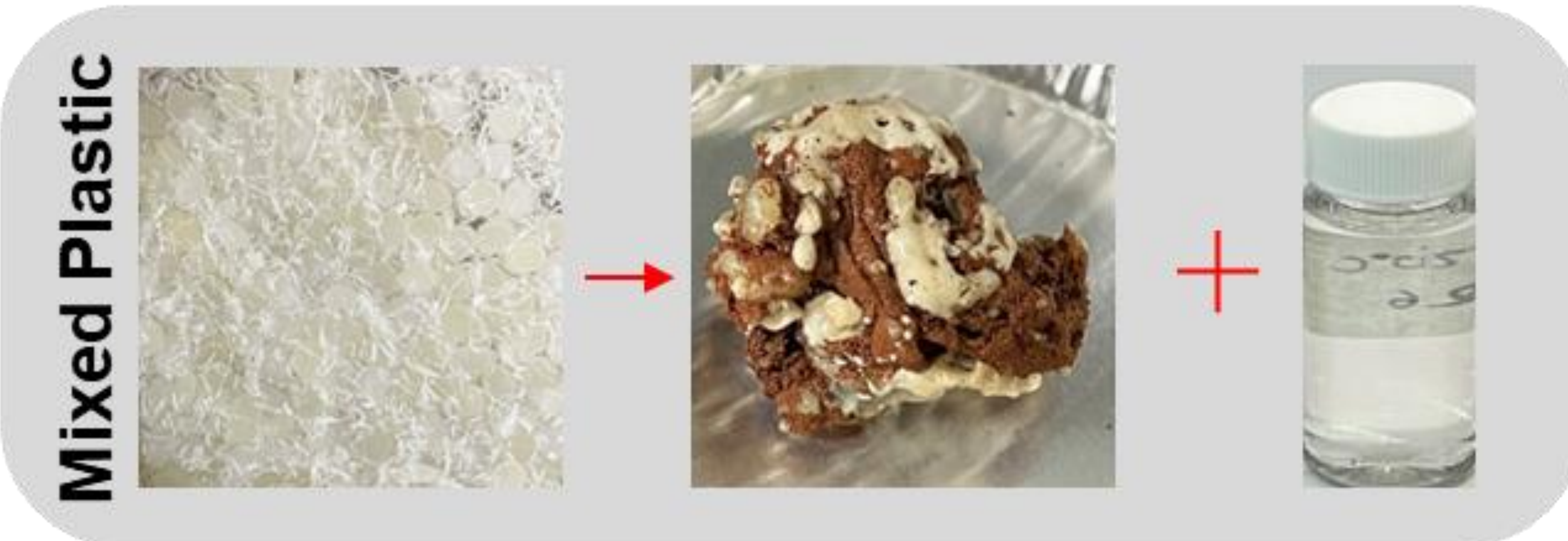
- **Mass yield = residual mass / original mass**
- **Majority of mass loss attributed to HCl elimination**
- **At low temp (220°C) H_2O_2 performs best**
  - >90% DE
  - Comparable to 240°C autothermal (>95%)
- **H_2O_2 > HCl > Autothermal > Base for pure PVC processing**



DE of HTT at different conditions, 200°C (blue), 220°C (orange), 240°C (red)

Objective Achieved: >99% removal of Cl in pure PVC

HTT of Mixed Plastics



Mixed Plastics

- **Produced surrogate mixtures**
  - PE, PP, PS, PVC
- **Reaction enhancers to lower temperature**
- **DE same as PVC, other plastics melt**
  - Unaffected by hydrothermal treatment up to >240C
  - H_2O_2 reacts with plastics

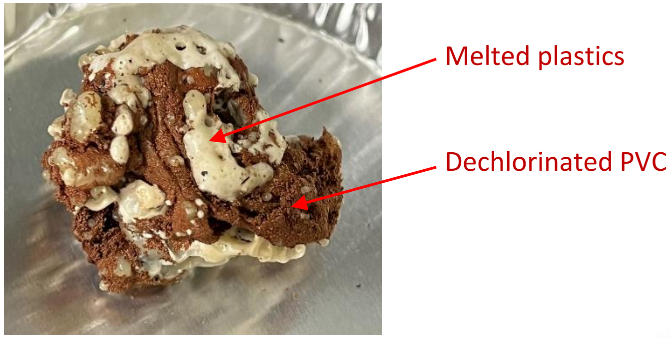
Surrogate Compositions

Component	PVC	Mixed Plastic
Paper		
Polyethylene		60%
Food (rice)		
Textile (cotton)		
Polypropylene		19%
PVC	100%	17%
Plant Waste (pine)		
Polystyrene		4%

Dechlorination Efficiency

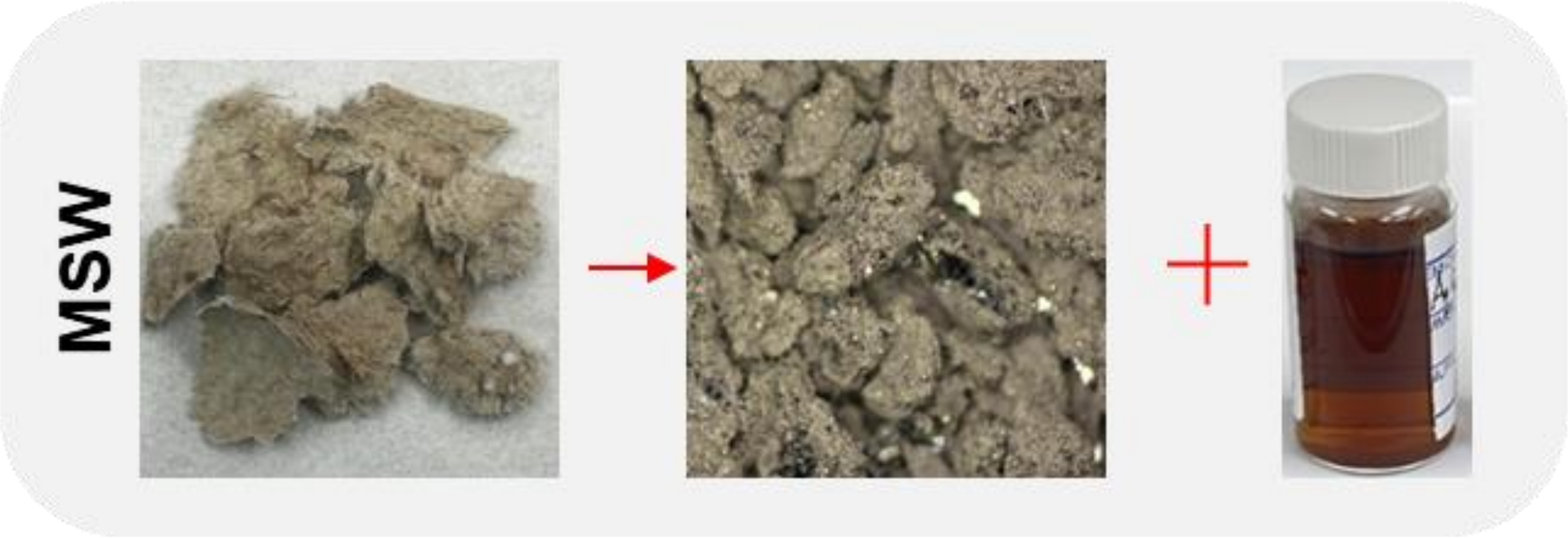
	Pure PVC	Mixed Plastic
Autothermal	100%	89%
H_2O_2	>90%	95%

HTT PE



HTT Mixed Plastic

HTT of MSW



MSW

- Assumed glass and metals removed
- Produced surrogate mixtures
- Same experiment procedure
- Reaction enhancers to lower temperature (H_2O_2, HCl, Base)

MSW Component	%
Newspaper	2.3
Glass	8.2
Aluminum Cans	1.1
Plastic Bottles	4.8
Steel Cans	1
Corrugated Paper	10.3
Office Paper	4.4
Yard Trash	1.1
Other Plastics	15.5
Ferrous Metals	1.7
Non-ferrous Metals	0.9
Other Paper	21.9
Textiles	5.1
C&D	7.5
Food	7.5
Misc.	6.7

Actual MSW

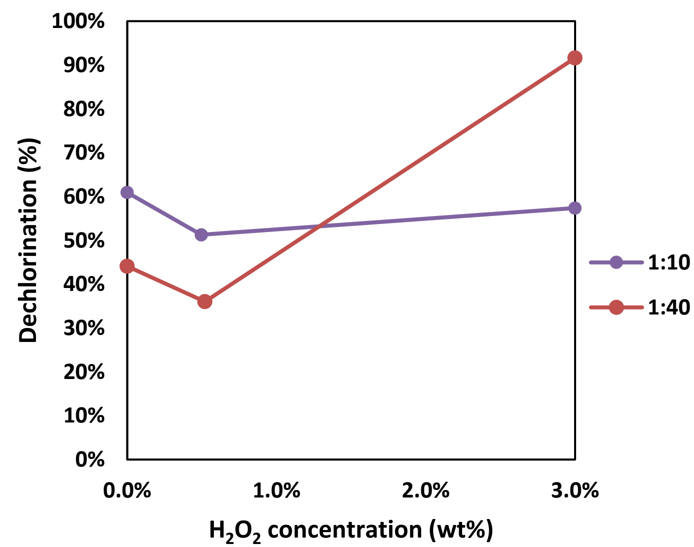
Component	PVC	Mixed Plastic	MSW
Paper			53.4%
Polyethylene		60%	16.6%
Food (rice)			10.3%
Textile (cotton)			7.0%
Polypropylene		19%	5.4%
PVC	100%	17%	4.6%
Plant Waste (pine)			1.5%
Polystyrene		4%	1.2%

Surrogate MSW

MSW slurry

HTT of MSW with H_2O_2

- **Issues reacting with MSW**
  - Tested various ratios (mass solids:mass solution) and H_2O_2 concentrations
- **Decomposes waste**
  - Up to 70% mass lost
  - Plastics destroyed
  - Suspended solids only recoverable by filtration
  - Greater Cl concentration in products
- **Higher pressures due to O_2 production**
- **Benefits cancelled out for MSW processing applications**



HTT Slurry

HTT of MSW with starting HCl

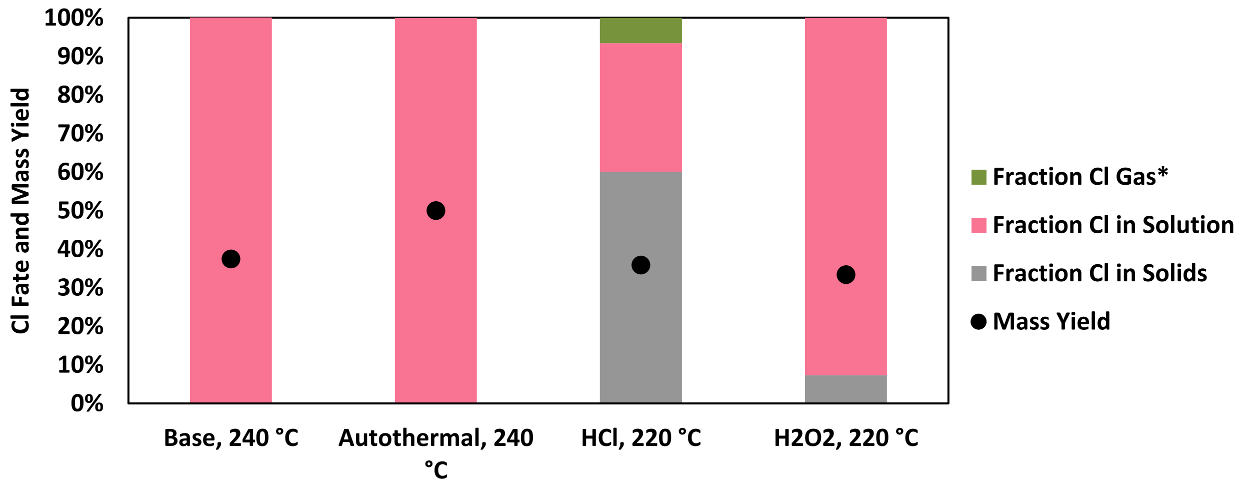
- **Targeting autocatalytic effects observed for pure PVC dechlorination**
  - Unsuccessful in lowering temperature required
- **Causes high mass loss, digestion of solids**
  - Bad for chlorine concentration in products
- **Enhances corrosion to steel**

Corrosion on stirrer (left) and aqueous fraction (right) from acidic conditions

- **More realistic / comparable to a continuous system where acidic water is recycled**
  - How to handle HCl produced in scaled-up system?

HTT of MSW

- **Base and autothermal had >95% chlorine removal**
- **Autothermal conditions maximized dechlorination and minimized mass lost**
- **Base did not inhibit reaction at low Cl concentration**
- **Conditions chosen**
  - Best results from pure water at 240 C
  - Base can be used to neutralize recycled water

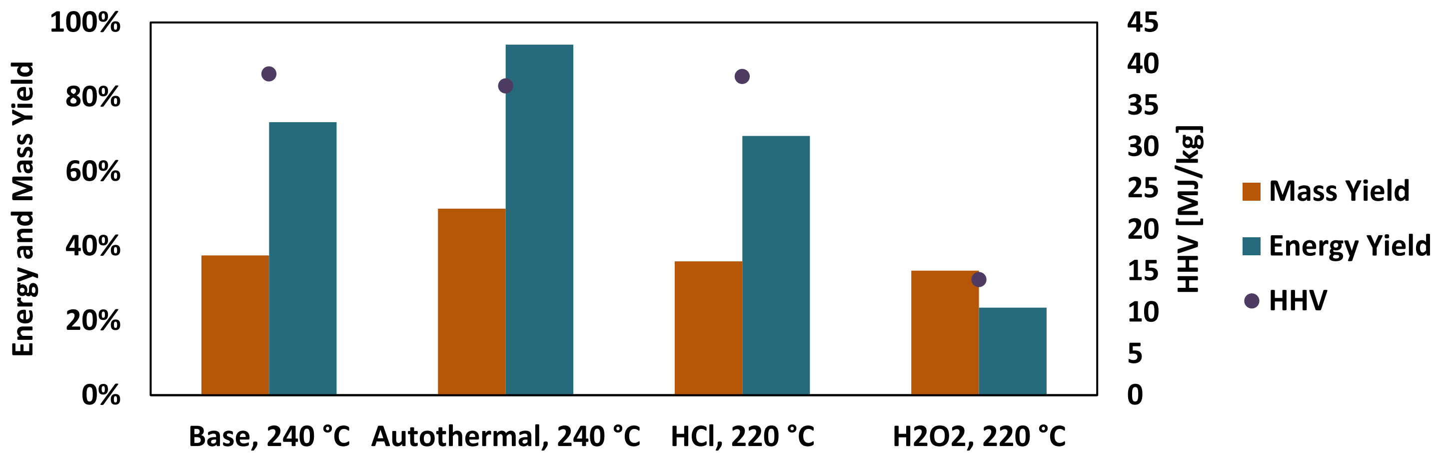


Objective Achieved: >99% removal of Cl

- Complete dechlorination at 240 C in <2 hour
- No detectible Cl in solids (by elemental analysis)

HTT Products Heating Value

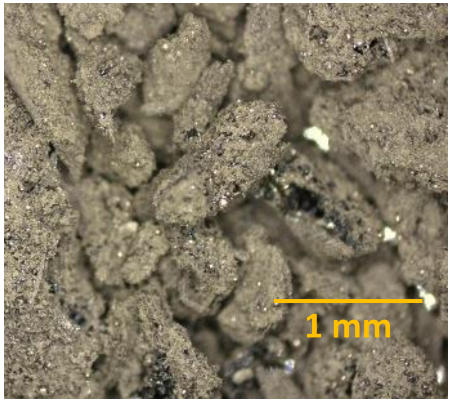
- **Energy yields** = $(HHV_{final}/HHV_{initial})$x(mass yield)
  - Higher heating values (HHV) measured with O_2 bomb calorimetry
  - Energy retention favors autothermal
- **Energy densification**
  - Raw MSW has HHV of ~<u>20 MJ/kg</u>, treated MSW has HHV of ~<u>37 MJ/kg</u>
    - 180% of original energy density
  - HHV greater than anthracite grade coal



Objective Achieved: 94% energy retained at 80% densification

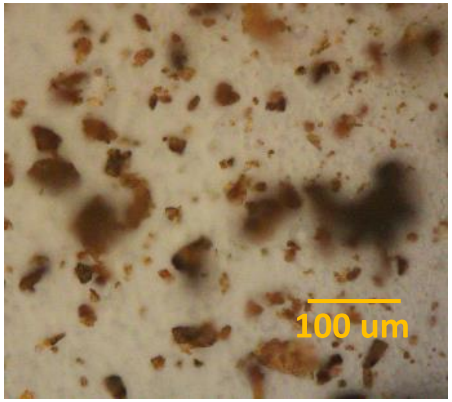
Products – Usability/Transport

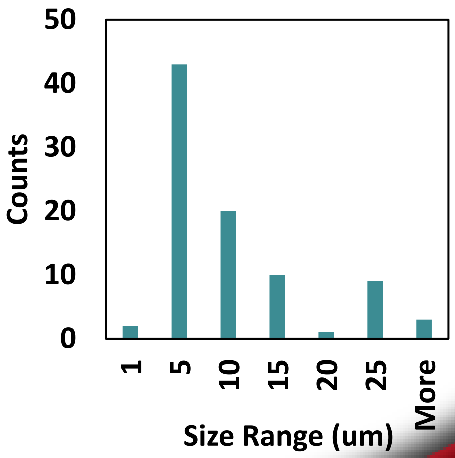
- **Less chlorine than coal** (<0.1-0.2 wt%)
- **Char products readily grind to fine powder**
  - EFG requires particle sizes of <100um
- **Density of HTT products were up to 3x MSW** (156 kg/m^3)
  - Raw: 144 kg/m^3, Ground: 250 kg/m^3, Compacted: 470 kg/m^3
- **Improved volumetric energy density**
  - Raw MSW: 3.1 GJ/m^3, HTT MSW: 17.6 GJ/m^3, Anthracite: ~27 GJ/m^3



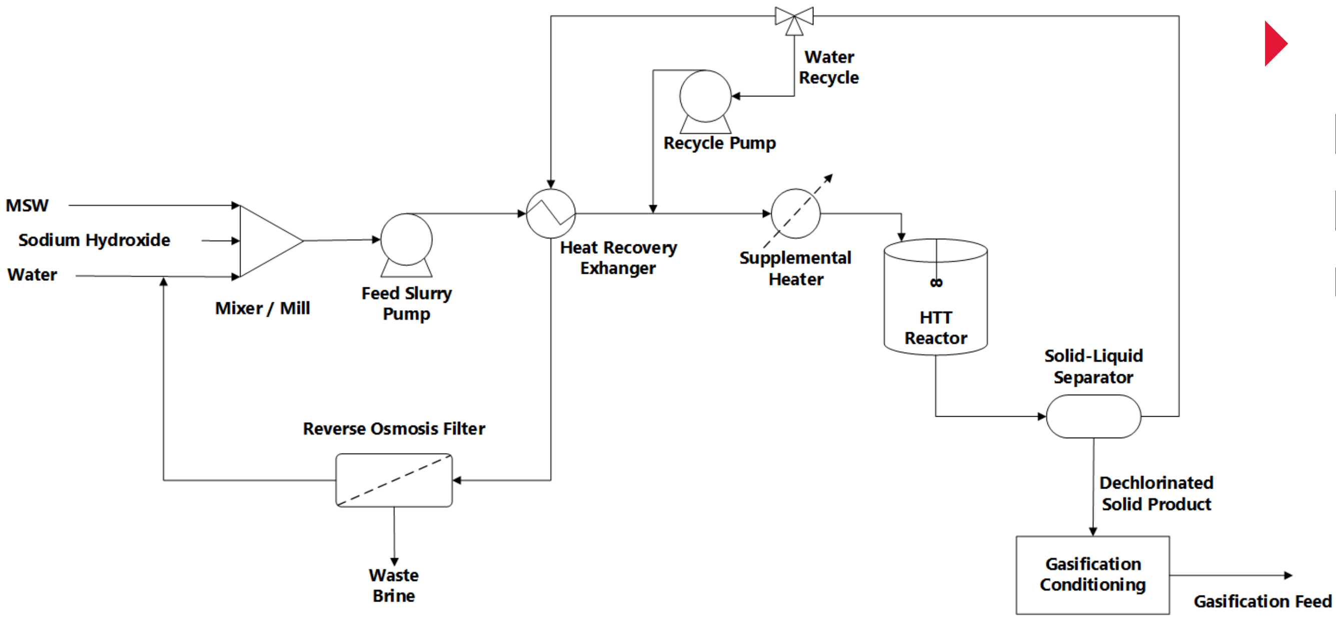
HTT MSW

Ground HTT MSW



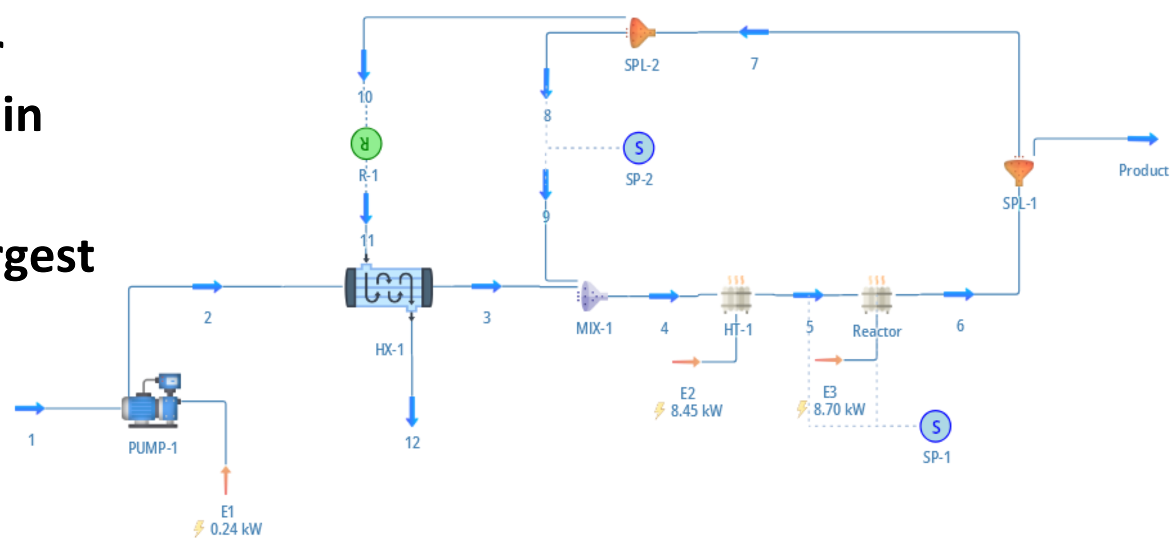


PFD and Process Model



- **PFD of the proposed process (left) and preliminary modeling (below)**
  - Basis for TEA, equipment and energy costs

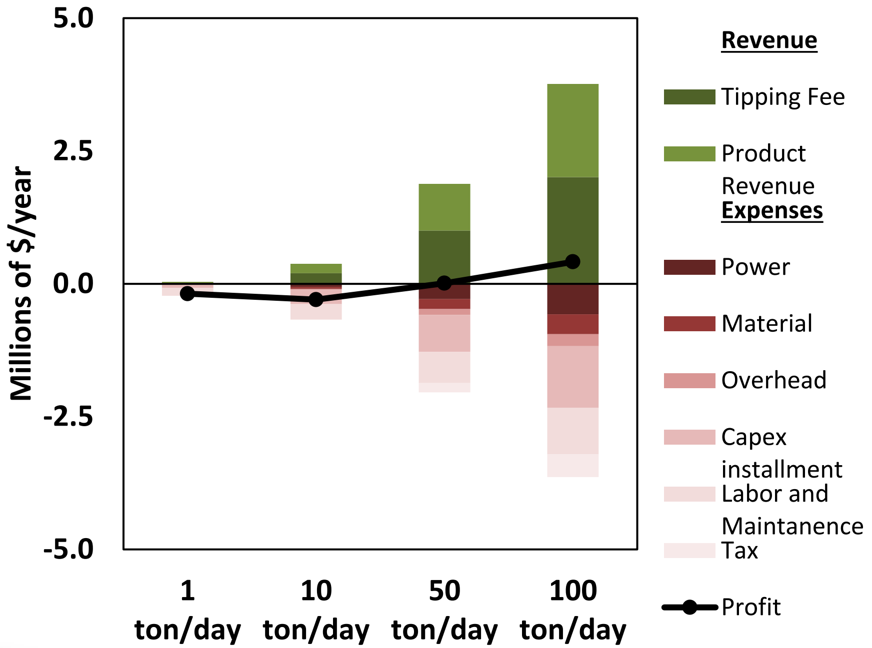
- **Base added to allow water recycling and maintain pH in desired range**
- **Reusing water saves on largest material cost**



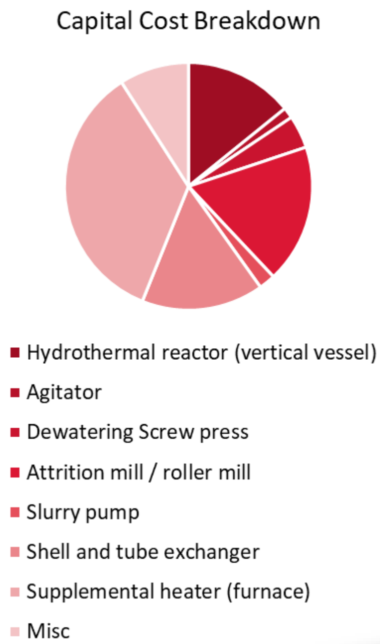
Technoeconomic Analysis

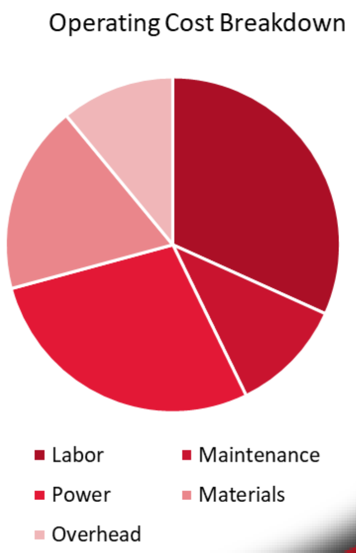
- **Analysis on 1, 10, 50, and 100 ton/day scales** (dry MSW basis)
- **Product priced to compete with energy equivalent to coal**
  - Same $/MJ, lower chlorine concentration
- **Profitable >50 tons/day**

Objective achieved: operating costs <$100/ton



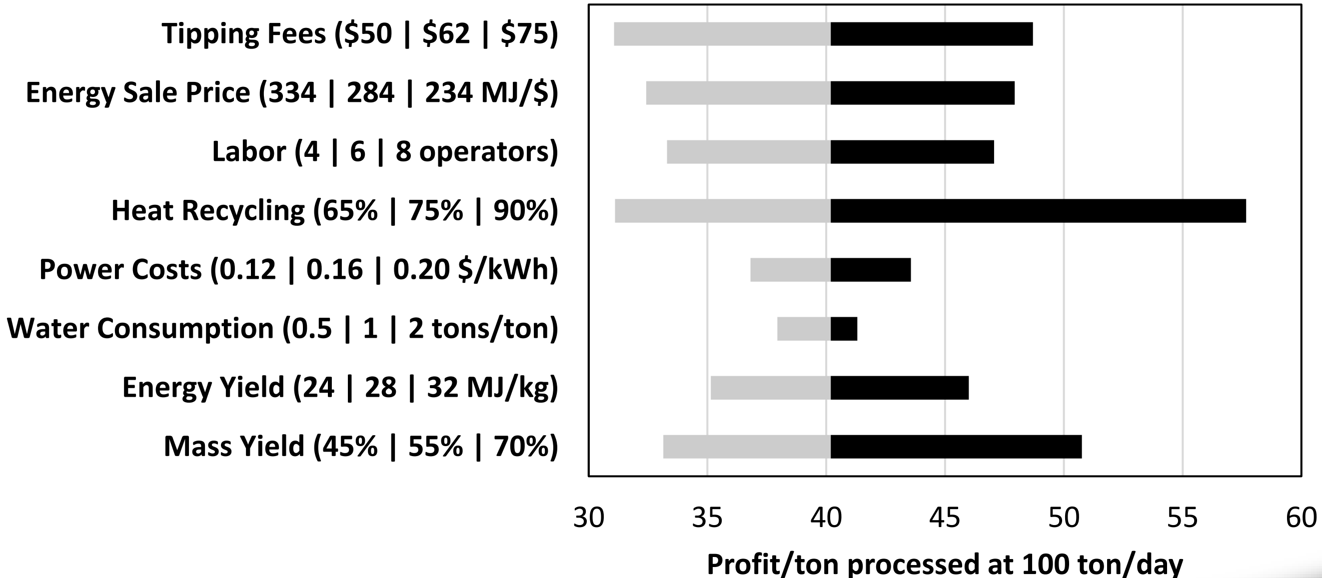
Net income analysis





TEA Sensitivity Analysis

- **Top 8 most sensitive factors evaluated**
  - low | expected | high
  - Total range $-5 to +$110
- **Heat recycling most controllable**
  - Integrated waste heat increases expected profit to >$60/ton
- **Payback period is <3 years with 5-year amortized capital costs**



Pricing/cost sensitivity analysis

Conclusions

- **Achieved key objectives:**
  - >99.9% chlorine removal from PVC, mixed plastics, and MSW
  - >94% of inlet energy content at 180% densification
  - Feasible operating costs and overall process economics for viable scale-up of HTT dechlorination

- **Future Work:**
  - Design, build, and characterize a continuous process
    - Optimize process with focus on pH control, residence time, and concentrations to Prove gasification performance of HTT material
  - Troubleshoot anticipated challenges: slurry heat exchanger, dewatering at pressure, recycling loop
  - Scale up and commercialize process

- **Thanks!**

References

- [1]Lan, K., et al., Feasibility of gasifying mixed plastic waste for hydrogen production and carbon capture and storage.*Communications Earth & Environment* 2022, *3* (1), 300.
- [2]https://www.penflex.com/chloride-chlorine-levels-and-stainless-steel-alloy-selection/
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