Wet-Air Oxidative Regeneration Process for Regenerating Poisoned Catalysts

Colin Anson, Ph.D. Senior Researcher Virent, Inc. September 12th, 2024



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Virent: Creating Opportunities for Renewable Markets



- Headquartered in Madison, WI
- Founded in 2002
- A wholly-owned subsidiary of Marathon Petroleum Corporation
- Multiple pathways in development
- Commercial focus is on scale-up and first plant deployment
 - Virent working with Johnson Matthey (JM) on commercial plant project to produce biofuels from sugars



BioForming[®] Process – Sugars to Aromatics

The S2A platform can work with a **range of sugar feedstocks** to produce **drop-in products** which can be blended with existing fuel product or refinery streams



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HYD - Sugar Hydrogenation

Industrial Uses and Virent's Approach



- Virent hydrogenates sugars to sugar alcohols to increase thermal stability in HDO step
- Industrially, a semi-batch process with Ni catalysts is used to produce sorbitol¹
- Continuous studies with Ru catalysts show higher performance than Ni catalysts
- Virent's tests with corn sugars showed catalyst deactivation

Sulfur Poisoning of Ru-catalyzed Hydrogenations



Literature review suggested sulfur may be causing deactivation



Fig. 8. Effect of cysteine and methionine addition on LA conversion at base-case conditions (Table 2): \blacktriangle , 50 ppm cysteine; \square , 1000 ppm cysteine; \diamondsuit , refined LA; \bigcirc , 130 ppm methionine; \triangle , 100 ppm cysteine. Vertical bars at 24 and 60 h denote change in feedstock composition.

Zhang et al. Bioresource Technol. 2008, 99, 5873-5880.



Figure 10. Effect of sulfur in bio-oil A in their hydrogenation performance. The hydrogen consumption, hydrogen-to-carbon ratio, and carbonyl contents of two hydrogenation tests using bio-oil A feed with different sulfur content. Reaction conditions: 160 °C, 1500 psig, 0.40 L bio-oil/L catalyst h, 2500 L hydrogen/L bio-oil.

Wang et al. ACS Sust. Chem. Eng. 2016, 4, 553-5545.

Sulfur frequently identified as a poison (typically through doping studies), but no catalyst regeneration procedures indicated

Other references:

- Glucose hydrogenation (Arena, Appl. Catal. A: General, 1992, 87, 219-229 and Elliott et al. Appl. Biochem. Biotech. 2004, 113-116, 807)
- Levulinic acid hydrogenation (Genuino et al. ACS Sustainable Chem. Eng. 2020, 8, 5903)
- Furfural hydrogenation (Li et al. Energy Fuels 2017, 31, 9585)

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H₂O₂-Based Regeneration of S-Poisoned Ru



Mild oxidative treatment effective at recovering activity

Liquid Hourly

Space Velocity

(LHSV)

Time (hr.)

14-24 hr

6-12 hr

4-10 hr

6-24 hr



Comparison of Methods for Regeneration of Raney Ni-Catalyst

 H_2

Pressure

No.

No.

1200 psi.

No

Catalyst

Activity

Recovery (%)

< 10%

0%

80%

30% DS, 10% DP, 7 ppm of sulfur.

Catalyst reduced under 1200 psi H₂, for 4-24 hrs, at 140° C, and 200° C, LHSV = 1

90-95%

- S poisoning in gasification of EtOH with Ru/C
- Regeneration of catalyst with H₂O₂ at ~100 °C recovers activity and selectivity
- Prolonged contact with H₂O₂ leads to cracking of support and loss of mesopore surface area

Dreher, M. Steib, M.; Nachtegaal, M.; Wambach, J.; Vogel, F. ChemCatChem, 2014, 6, 626-633.

| • | Ni- and Ru-catalyzed hydrogenation of sugars |
|---|--|
|---|--|

 Regeneration with H₂O₂ recovers significant catalyst activity

Treatment

70° C. wash

Bleach wash

 170° C, wash

Reaction condition:

H₂O₂ wash

Feedtock:

Virent's Implementation of H₂O₂-Based Regenerations

Regens conducted at moderate conditions with low [H₂O₂]



Time

- Extended run showing positive impact of H₂O₂-based regenerations
 - Sulfur detected in effluent by ICP
- Upon emptying reactor, large amount of catalyst fines and weakened extrudates from carbon support
 - Damage presumably caused by H₂O₂ (as observed by Vogel et al)

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Developing Milder Regeneration



Wet Air Oxidative Regeneration (WAOR)

- Virent hypothesized that using O₂ and water may provide a milder regeneration method
- Limit catalyst degradation and no need for H₂O₂ storage



Proof of Concept: 4 successful regenerations using 1% O₂ with no observed catalyst damage

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Blommel, B.; Anson, C.; van Straten, M.; Steenwinkel, E.; Holland, C.; Gearing, R.; Ferguson, C.; Wild, R.; Campbell, I. Systems and Methods for Wet Air Oxidative Regeneration of Catalysts. US 2023/0072588 A1. Published Mar. 9, 2023.

Improving Commercial Viability



High N₂ usage hurts economics of regeneration procedure

- While WAOR conditions are mild, can still cause support degradation
- To understand the impact of temperature and O₂ partial pressure, performed regenerations on "clean" catalysts



- Size of circles correlates with rate of CO₂ formation
- pO₂ calculated from O₂ composition, H₂O vapor pressure, and reactor pressure at given temperatures
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Extended Catalyst Stability



Regenerations using pure air and mild conditions



- Extended stability run over 13 regenerations shows good recovery of catalyst activity
- Unloaded catalyst did not show cracks in structure and maintained good mechanical strength

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Deploying WAOR on Demonstration Scale JM otin



- Production Unit controlled to hit a target HYD conversion to feed forward, so temperature used to control process
- High temperature leads to caramelization + fouling, requiring periodic regenerations
- System successfully completed >5 WAORs, further development on-going
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Thank you!

Colin Anson Senior Researcher colin_anson@virent.com

