Synthesis of Acetic Acid Via CO2-CH4 Reformation and Carbonylation of Methanol

Team G – Stephan Grunwald, Devin Metzger, Sean Buchanan, Christopher Kleiman

Scope Definition & Design Basis

The purpose of the project was to design and evaluate the economic feasibility of the production of Acetic Acid utilizing an available CO_2 feed.

The recommend design must meet the following:

1) Production of 250,000 lb/hr of Acetic Acid (AcOH).
2) There must be no emissions of CO_2 from the process.

Initial Design Considerations

The production of acetic acid utilizing the available CO_2 stream consisted of two primary reactions, i.e. methane reformation and methanol (MeOH) carbonylation.

Reformation:

- Conversion of CH_4 vs. CO_2 reactant cost minimization of CO_2 utilization.
- Catalysts selection to minimize coke formation, cost, and to maximize CH_4 conversion. Comparison of Ru, Ni, Pd & different supports
- Various CO_2/CH_4 molar feed ratio and effect on coke formation and conversion.
- Reactor Temperature effects on conversion
- Reactor Pressures effect on conversion

Carbonylation:

- Catalyst, promoter and co-catalyst choices impacted CO utilization, reaction conditions and process economic feasibility
- Any catalyst/co-catalyst must be recycled completely or nearly completely as to mitigate environmental risk and economic impact
- Catalyst choice also had large influence water gas shift reaction (WSGR), a major side reaction
- CO_2 could not be released from process, therefore the WGSR needed to be limited
- Presence of water in reactor necessary to ensure no drying out of catalyst
- Major by-products were propionic acid and acetaldehyde
- Product separation and purification to achieve desired purity

References

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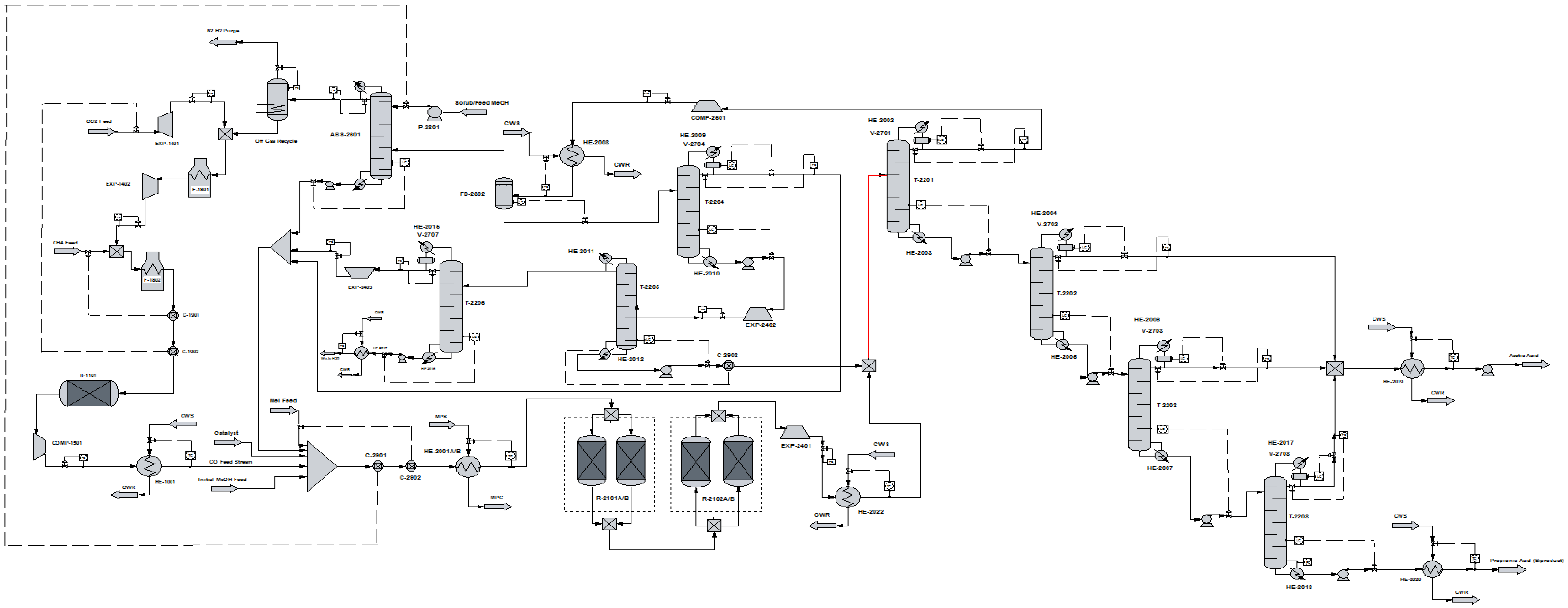
[3] Department of Chemical Engineering, Auburn University, Design of a Process for the Production of Fuels and/or Chemicals from Hydrocarbon Feedstocks. http://wp.auburn.edu/eden/wp-content/uploads/2012/03/4470_Project_ Description-2013.pdf (accessed January 2015).

[4] Seider, W.D.; Seader, J.D.; Lewin, D.R.; Widagdo, S. Product and Process Design Principles: Synthesis, Analysis, and Evaluation, 3rd Edition, John Wiley & Sons.



Key Streams: Products and Feeds

Feed Streams

Stream	CH_4	CO_2	MeOH
Rate: lb/hr	39,000	82,500	147,000

Product Streams

Stream	Acetic Acid	Propionic Acid	Purge Stream
Rate: lb/hr	254,000	200	126,000

Catalyst Load

Stream	Methyl Iodide Co-Catalyst	Iridium Catalyst
Load: lb/hr	345,000	1,400

Economics

- The Total Capital Investment for the recommended process is about $145 million.
- The annual incremental costs and utility costs are $90 million and $62 million, respectively, when at full capacity.
- When at capacity, the annual raw material costs are found to be $221 million and waste water costs are $23 million.
- A 10-year ROI of 15% was used to determine a minimum required selling price of $436/ton for acetic acid.
- The payback period is roughly 3.67 years.

Design Strategy

Reformation of CH_4

- Determination of the reaction conditions involved the selection of the temperature, catalyst, pressure, and CO_2/CH_4 feed ratio
- Catalysts investigated included those of noble metals Ru, Ni, and Pd in which all will form carbon deposits overtime leading to catalyst deactivation
- Catalyst selected was Ni due to its relatively lower cost than the other noble metals and lower degree of coking that Pd
- Reaction temperature, pressure, and CO_2/CH_4 feed ratio were simulated by Sun et. Al, where these parameters were optimized individually to maximize the conversion of CH_4 through the iteration of the parameters described
- Reaction conditions selected for the optimized process of a Ni-Al_2O_3 supported catalyst, 1472°F, 14.7 psig and CO_2/CH_4 feed ratio or 2/1
- Optimized reaction parameters produced X_{CH4} conversion, CO + H_2 productivity, and CO/H_2 product ratio of 97.64%, 1.41 and 1.26, respectively

Carbonylation of MeOH

- Major MeOH carbonylation processes considered: Cativa™ and Monsanto
- Monsanto process catalyzed by Rhodium (Rh, cost ≈ $1,175/troy oz) at OP conditions of 425 – 855 psig, 302 – 392°F and ≥ 10 wt% water
  - CO utilization ≈ 84%
- Cativa™ (chosen) process catalyzed by Iridium (Ir, cost ≈ $575/troy oz) and methyl iodide (MeI) at OP conditions of 200 psig, 347 - 392°F and ≈ 4.5 – 5.5 wt% water
  - CO utilization ≥ 94%
  - 30% lower overall CO_2 emissions
- MeI soluable in feed MeOH/water mixture and allowed for feed to be used as absorbing liquid to recover co-catalyst MeI
- Ir catalyst soluable in MeI, therefore was recovered with MeI
- Feed costs reduced via MeOH, CO, CO_2 and methane recycle
- AcOH product lost by initial separation recycled and recovered to product during MeOH purification
- Enough propionic acid produced to justify purification and sale

Future Work

The following are recommendations made by the design team that would further improve the process feasibility. These changes came after the process design was finalized and should be considered for any future process development.

- Consideration of multiple reactors to allow for online catalyst regeneration
- Examine the need for a CO_2 purge to limit the presence and potential build up of nitrogen and hydrogen
- Further study the reaction kinetics of the reformation reactor and detail the effects of catalyst degradation on the system
- Conduct further research on the catalyst (IrI_3) to fully understand solubility, effectiveness, and age pattern
- Reevaluate holding periods of materials to follow industry standards to better gauge storage requirements
- Additional research on material selection to ensure proper material usage for equipment throughout the system
- Conduct scale up studies to examine the byproduct reactions and determine their actual presence in the system
- Examine the design of an Emergency Relief System that can properly treat flushed gasses in times of emergency
- Examine the effects of CO_2 internal transfer fees and AcOH pricing on economic returns