29th Annual Meeting of the
Chemical Reaction Engineering Laboratory (CREL)
at
Washington University
St. Louis, Missouri

Novel Ideas for Liquid Hydrocarbon Oxidations

Higher productivity, selectivity and yield can be achieved with use of pure oxygen and oxygen enriched air.

To document these advantages CREL proposes to

- Test the effect of increased oxygen concentration (via increased pressure using enriched air, using pure oxygen, using solvents with high oxygen solubility) on productivity and selectivity in microreactors to eliminate safety constraints.
- For most promising system develop appropriate reactor technology
- As an example, consider needed development for terphtalic acid.

Oxidation Reactions for TPA Via Liquid Oxidation Reactor (LOR)

Praxair and Shell Patents (CREL Patents)

2003 CREL Annual Meeting

Chemical Reaction Engineering Laboratory
Washington University

Introduction

- Liquid-phase oxidation of hydrocarbons has a wide range of applications in the production of a number of industrial chemicals and intermediates (e.g., terephthalic acid (TPA), adipic acid (ADA), phenol, polyethylene terephthalate (PET), nylon 6.6, caprolactam, bisphenol A, etc.
- Air is a conventional source of oxygen gas in the majority of such oxidation processes.
- Air is usually dispersed into the reactors via axial flow impellers or gas spargers.

Advantages
Air-Based Oxidation Technology

- Abundant and cheap oxygen gas supply
- Inherent means of removal of part of the reaction heat from the reactor due to associated nitrogen gas
- Prevention of buildup of residual oxygen concentration within the reactor

Disadvantages

Air-Based Oxidation Technology

- Air contains much inert nitrogen gas which lowers volumetric productivity and causes high gas flows.
- The reactor vent gas contains significant amount of solvent and reactants vapor entrained in the gas stream.
- The recovery of such organic chemicals from the gas requires an extensive chemical treatment before the gas is discharged into the atmosphere.
- The low concentration of oxygen in air impairs oxygen solubility, reduces the oxidation rate and causes high reaction times and large reactors.

Motivation

- **To overcome the disadvantages of the air-based oxidation process, pure oxygen or oxygen enriched air has been proposed (Praxair patents). A novel catalyst that does not require the presence of halide promoters (e.g., bromine) has been proposed (Shell patent) which reduces significantly the cost of the construction material.**

  Advantages

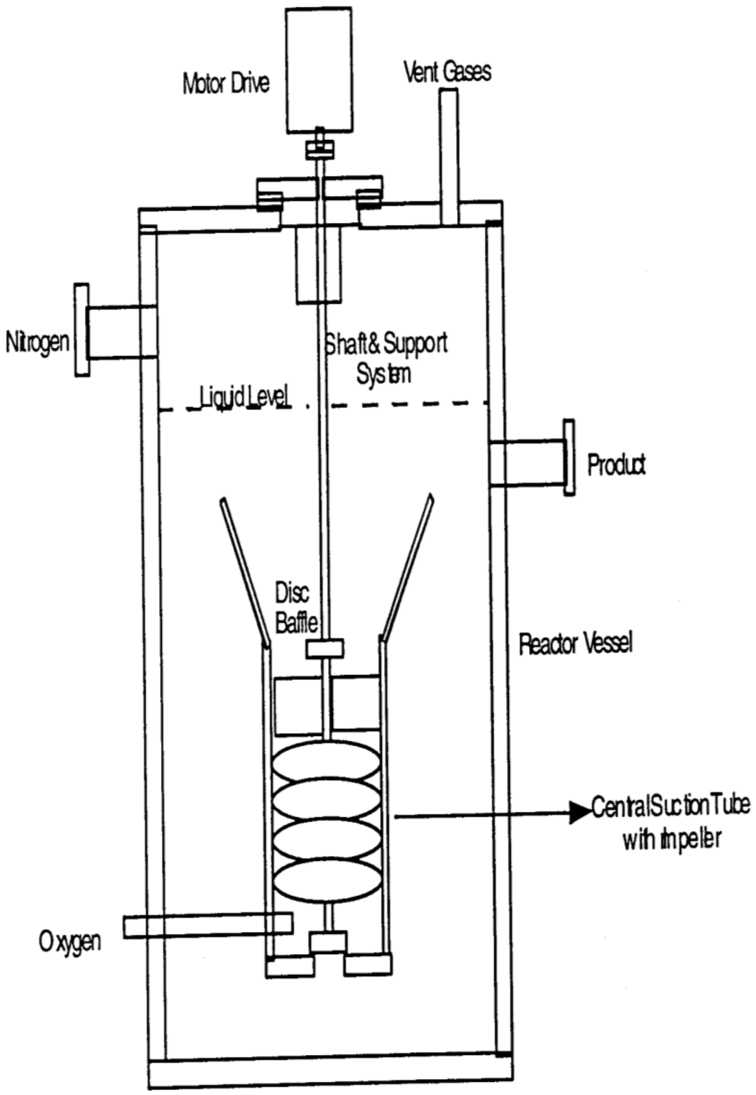
  - **Significant reduction in the amount of the reactor vent gases, lower losses of solvent and reactants and hence need for smaller treatment plant.**
  - **Reduction in the power requirement for compression (through the oxygen-based operation raises the raw material costs).**
  - **Increased partial pressure of oxygen in the gas allows reactor operation at lower pressure and hence lower reaction operating temperature.**
  - **Lower temperature reduces the solvent and reactant burn-up into undesirable by-products like CO, CO2.**
  - **Increased partial oxygen pressure results in an enhanced absorption rate of the gas in the liquid phase which accelerates the reaction rate.**
  - **Reaction rate, conversion and selectivity of the desired product are improved.**
  - **With an improved reaction rate, a given conversion can be achieved in smaller-sized or fewer reactors.**
  - **All above leads to a net saving in terms of capital investment and operating costs.**

- **However, the use of oxygen in the hydrocarbon liquid-phase oxidation has safety and flammability concerns. This prevents its widespread commercial use to date for organic chemicals despite its widespread use in the manufacture of inorganic chemicals.**

Current Status

Oxygen and Oxygen-rich Gas Based Oxidation Technology

- Praxair claimed, through a series of patents, technological developments in the design of the oxidation reactor and gas dispersion system which allow safe reactor operation with high purity oxygen.
- This technology, known as liquid oxidation reactor (LOR), is now available for license in the production of TPA and other organic oxidations.
- Dow (previously Union Carbide) currently operates LOR technology commercially at Texas City, TX to produce "Oxygenated Organic Intermediates". As a part of the capital saving they use one LOR instead of 3 comparable sized air based reactors.
- Oxygen carries a higher cost and a greater safety risk. Therefore, the benefits of an oxygen-based process must overcome the additional costs and risks.
- LOR technology overcomes these costs by providing both capital and operating savings. The magnitude of these savings is process-dependent.



Capital Savings

Pure Oxygen and Oxygen-rich Gas Based Oxidation Technology

- LOR eliminates the need for the main air compressor (both capital and operating savings)
- LOR dramatically reduces the sizes of the vent stream between 60% to 90% and the cost of all vent stream treatment equipment.
- LOR reduces the size and cost of the reactor by about 10% to 20%.
- For cases in which the chemical kinetics are sensitive to oxygen concentration, LOR can provide much greater reduction in reactor volume for the same level of production (DOW (Union Carbide) example).
- The capital savings associated with a world scale PTA Plant are about $30MM.

  $12 MM – from elimination of the air compressor.

  $2.5 MM – for the reactor

  $2 MM – in vent treatment reduction

  $13.5 MM – for installation, unscheduled costs and contingencies.
- Implementing Shell catalyst (Shell patent) will further increase the capital saving by reducing the cost of the construction material.

Operating Saving

Pure Oxygen and Oxygen-rich Gas Based Oxidation Technology

- Process-dependent
  - In some processes, selectivity improvements are significant.
  - In others, reduction in solvent loss is the primary benefit.
- In TPA, operating savings result from
  - Reduction of acetic acid losses
  - Yield improvement
  - Reduction in energy requirements

  These offset the cost of oxygen.
- Raw materials and utility costs vary with location and time.
- At 2000 Gulf Coast prices, Praxair expected the net operating savings to be $1MM/yr to $2MM/yr.

Safety

Pure Oxygen and Oxygen-rich Gas Based Oxidation Technology

- Safety is an obvious concern in adding oxygen to hydrocarbon liquids. LOR technology approaches process safety by mitigating the risks associated with the process.
- There are <u>three areas</u> of risk that need consideration:
  - Oxygen injection (Flow interlocks and sparger design and safety)
    - Positive pressure is maintained to avoid backflow of organic liquid.
    - Loss of oxygen pressure and other factors will trip emergency shut down (ESD) procedures that include discontinuing the flow of oxygen and maintaining positive pressure by initiating nitrogen flow.
    - Sparger must be constructed of materials compatible with both the acetic acid solvent and oxygen at the process temperatures and pressures.
  - Within the reactor, individual bubbles may be flammable, but a bubbly flowing liquid cannot propagate a detonation, even if a source of ignition is present.
  - The head space. The residual oxygen-fuel mixture reaching the headspace must be diluted with a nitrogen purge.
  - A dual purpose purge is used with one flow set for normal operation and a much higher flow for ESD.
- Praxair has a rigorous process hazard analysis and safety procedure as a part of commercialization at DOW (Union Carbide) which are accessible to CREL for TPA patents.

TPA Current Status

Market

- Worldwide installed capacity for TPA in 1997 was 19.3 million metric tons per year.
- Long term capacity growth is expected to slow to about 6% per year from historical rate of 8% per year due to the recent significant additional TPA capacity, particularly in Asia.

The Major Licensors of TPA

BP (previously Amoco), Inca (a Dow subsidiary), DuPont (ICI Technology), Eastman, Mitsui.

BP holds a leading position.

TPA Current Status (continued)

Technology

- The BP process is based on liquid phase oxidation of paraxylene with air in stirred tanks.
- The technology was originally developed by Mid 20th century.
- Manganese and cabolt acetate catalyst plus a bromine promoter are used (Temperature ~ 170-225 °C, pressure 100 – 300 psig)
- Variations of the BP process have been developed by DuPont (ICI previously) Inca, Eastman and Mitsui.

CREL Patents

Praxair Patents

- The know-how of LOR technology and its hazard analysis and safety are available to CREL. 1 gallon LOR experimental set-up was given to CREL by Praxair.

US 5,371,283 (Dec. 6, 1994) **Terephthalic Acid Production**

US 5,371,283 is the earliest of the TPA patents. It covers both sub-cooled and evaporatively-cooled operation. It provides for an improved process for producing terephthalic acid by oxidation of p-xylene with oxygen or an oxygen-rich gas by oxidation in a mechanically-agitated reactor. A wide range of reactor operating conditions is covered.

Conditions: Pure oxygen or oxygen enriched air containing at least 50% oxygen
Temperature: 150°C to 200°C
Pressure: 100 psig to 200 psig
Residence time: 30 to 90 min
Catalyst: Cobalt and manganese as acetate and bromine
Solvent: acetic acid medium/water
Material of construction: titanium, Hastalloy C

CREL Patents (cont).

US 5,523,474 (June 4, 1996) Terephthalic Acid Production Using Evaporative Cooling

US 5,523,474 discloses an improved process for producing TPA using an evaporatively-cooled reactor and pure or nearly pure oxygen. The claims include coverage for recirculating the liquid using a draft tube and axial impeller system. Other details of mixing and gas injection are covered in dependent claims.

Conditions: Similar to the previous patent (US 537,283, Dec. 6, 1994)

US 5,696,285 (Dec. 9, 1997) Production of Terephthalic Acid With Excellent Optical Properties Through the use of Nearly Pure Oxygen as the Oxidant in p-Xylene Oxidation

US 5,696,285 discloses a method for producing an "aromatic carboxylic acid" and so expands the scope of coverage beyond TPA. Dependent claims specifically mention terephthalic acid, trimellitic acid, isophthalic acid, and dicarboxynaphthalene.

Conditions: Pure oxygen or nearly pure oxygen
Temperature: 180°C to 190°C
Pressure: 100 psig to 125 psig (most preferably 115 psig)
Residence time: 60 min (30 – 90 min is suitable also)
Catalyst: Cobalt and manganese as acetate and bromine
Solvent: acetic acid medium/water
Material of construction: titanium, Hastalloy C

CREL Patents

Shell Patent

Shell patent complements the Praxair patents for TPA production.

US 6,153,790 (Nov. 28, 2000)

US 6,153,790 discloses an improved process for producing TPA using at least 50% by volume oxygen enriched air with a catalyst system comprising zirconium and cobalt which can be in any form that is soluble in the reaction medium. The absence of halide promoters is therefore preferred which represents one of the additional advantages for TPA technology.

Conditions: At least 50% by volume oxygen enriched air
Temperature: 80°C to 130°C
Pressure: at least 1 psia oxygen partial pressure
Catalyst: Cobalt and zirconium in soluble form (e.g., organic acid salts, basic salts, complex compounds and alcoholates). The ratio of cobalt to zirconium is preferably greater than about 7:1 molar.
Solvent: acetic acid medium/water
Material of construction: 316 stainless steel

Proposed CREL Plan for Discussion with Potential Partners

- Combination of the Shell patent (catalyst), Praxair patents and Praxair LOR technology using oxygen enriched air or pure oxygen should lead to a purer product at higher yield and at higher rates while also bringing savings in materials of construction.
- A technology superior the BP and other processes can be developed based on such combination.
- The feasibility and the advantages of replacing the solvent with supercritical CO2 expanded solvent will be also investigated and evaluated. New and suitable catalysis for such solvents will be sought based on molecular scale computation and design as a part of NSF-ERC-CEBC research activities.
- To conduct and commercialize such a development, we would like to establish a partnership with a strong chemical company, or a mini-consortium of companies, to finance the needed R&D to establish the database for such technology that would lead to a pilot plant or a demo plant in return for a worldwide licensing rights with future small royalty payments to be made to CREL and/or CEBC.

CREL Tasks

- **The following is a tentative outline of tasks of work envisioned for such technology and process development:**

Task 1: Make LOR lab facility operational

Task 2: Combine LOR with Shell catalyst and confirm claims of product purity.

Task 3: Perform economical and environmental evaluation and feasibility analysis

Task 4: Explore various concentration of oxygen enriched air vs. pure oxygen with Shell catalyst, with Praxair patents catalyst and compare the results. Identify best conditions for yield and purity.

Task 5: Investigate the use of CO2 supercritical and mixture of CO2 supercritical and solvent (acetic acid) with both Shell catalyst and the catalyst used with Praxair patents. Develop a new catalyst based on the findings and based on the molecular scale computation and design.

Task 6: Develop kinetic models for the most promising investigated conditions.

CREL Tasks (continued)

Task 7: Investigate the reactor hydrodynamic parameters and flow field via flow visualization using CREL non-invasive advanced measurement techniques (computed tomography (CT) and computer automated radioactive particle tracking (CARPT)) and 4 point optical probe for bubble dynamic measurements.

Task 8: Develop mechanistic reactor model based on the measured flow field visualization and hydrodynamic parameters and the developed kinetic models.

Task 9: Address safety issues by modeling and experimental work.

Task 10: Develop safe scale-up procedures.

Task 11: Design and develop large pilot or demo plant

- **Tasks 1-9, can be achieved with a partner company or a mini-consortium funding.**
- **For Tasks 10-11, a sponsor or additional sponsors are needed if a partner company or a mini-consortium alone cannot fund these steps.**

Acknowledgement

CREL would like to acknowledge:

- Praxair and Shell for donation patents
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