## The Regeneration of Hydrocarbon Synthesis Catalyst

### A Partial Review of the Related Art Published From 1930 to 1952

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**HIMORE** 

# Literature Research Activities at Syntroleum

Review U.S. & foreign patents

ninoral

- pre 1960
- pre 1960-1980
- pre 1980 present

•Tom Reels

•Published Literature

#### How long can the horse run?



FT SYNTHESIS



Syntroleum

#### Technology developing with Cobalt Catalyst in Fixed Beds

- 1930 GB Patent 334,251 British Celanese Limited
- •Proposes deactivation due to tarry matter formed by minute amounts of high molecular weight by-products
- •Teaches use H<sub>2</sub> rich gases at T £ synthesis temperatures
- Teaches higher pressures preferred
- •Discovered activity of regenerated catalyst sometimes higher than fresh value
- •Claims applicability for other types of deactivation (including sulfur)

**INTRO LEU** 

#### GB Patent 486,928 Ruhrchemie (1938)

"It has long been known" that the effective life of the catalyst is longer when operated at lower temperatures. However, even at lower temperatures, catalyst life is still not sufficient.

#### **CLAIMED REGEN METHODS:**

- Periodic "in situ" solvent wash
- H<sub>2</sub> and/or gases or vapors such as steam
- Can operate at higher temperatures

## U.S. Patent 2,259,961 Whalley (1937)

Deactivation due to accumulation of wax and/or non-volatile products

- Describes solvent washing for regeneration
- •Hot gases can be employed for volatilization
- •H<sub>2</sub> treatment activates the catalyst

# Herrington & Woodward (1939)

Presents data showing H<sub>2</sub> more effective than inert gases

#### Catalyst yield

Aged	After N2 treat	After H2 treat
57.2	61.2	75.5

• Conclude that H<sub>2</sub> chemically interacts with the wax deposit responsible for deactivation

•Presents data confirming H<sub>2</sub>S or CS<sub>2</sub> irreversibly deactivates catalyst

•Data discussed in terms of carbide intermediate

#### U.S. 2,231,990 Dreyfus (1941)

**Regenerated Step Employs** 

Reduced pressure to vaporize wax-like deposits

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- Periodic pressure reductions at < 0.5 atm</li>
- Employs inert gas in lieu of reducing pressure

#### U.S. 2,224,048 Herbert (1940)

- Add inert synthesis gas to improve catalyst life (> 20 vol %)
- Recycled tail gas can be source of inerts
- Addition of "benzine" vapors to feed gas increases catalyst longevity
- Staged operations with higher pressure in latter stages
- Regenerate by periodically reducing pressure

#### U.S. 2,238,726 Feist & Roelen (1941)

- "paralyzing effect of the non-volatile reaction products deposited on the catalyst will be felt already after a few days."
- Remove deposits at regular intervals
- Extraction process conducted "in=situ"
- •"In-situ" treatment with  $H_2$  or  $H_2$ /steam at synthesis temperatures
- •Perform very frequently (up to several times per day)
- •Prefer using H<sub>2</sub> without any CO (but some CO acceptable)
- •Can employ solvent wash prior to H<sub>2</sub> treatment

#### U.S. 2,289,731 Roelen et al (1942)

Presents "new" H<sub>2</sub> based regen method

- H<sub>2</sub> passed over catalyst to remove deposits of paraffin hydrocarbons
- Other precipitates inducing inactivity are removed with continued H<sub>2</sub> treatment
- H<sub>2</sub> treatment conditions:
  - High H<sub>2</sub> flows (should employ recycle loop)
  - Oxygen containing constituents should be kept at very low values <1200 ppm<sub>v</sub>
  - Can ramp H<sub>2</sub> up to 450°C

Perform oxidation step prior to treatment with H<sub>2</sub>

- Allows better contacting of H<sub>2</sub> with catalyst
- Oxidized at temperatures > synthesis values

Solvent washing or H<sub>2</sub> /steam treatment at elevated temperatures are ineffective regen methods

**Patent teaches:** 

•Alternate exposure to feed gas with higher H<sub>2</sub> /CO ratio (>2.5)

•Catalyst does not have to be taken out of service

•Period of time under high ratio conditions is small fraction of on-stream time

**A** 



H2 TREATMENT

OXIDATION/ H2 TREATMENT



Syntroleum

#### Run Data of Hall & Smith (1946)

#### RRx [=] hydrogen treatment



RR

#### Catalyst steadily deteriorating

•EOR examination of catalyst does not reveal "adequate reason for final collapse" speculate alteration in catalyst surface or some strongly absorbed poison

Co supported on kiselguhr with thoria & magnesia

#### U.S. 2,360,787 Murphree et al. (1944)

#### Presents Process Configuration for CO Based Fluid Bed System

- Continuous regeneration with H<sub>2</sub> at 500°F
- Presents critical design basis for pressure balance
- Residence time requirements for continuous processing

#### U.S. 2,433,072 Stewart et al. (1947)

**Discloses ex-situ regeneration of slurry catalyst** 

- Separate catalyst from gas and liquid phase
- Treat with hydrogen or other method
- Recycle regenerated catalyst back into reactor



#### U.S. 2,478,899 d'Ouville (1949)

Presents regeneration method which does not destroy "layer of metal carbide or other active characteristic of catalyst"

- •Contact with H<sub>2</sub> at low (~50°C) temperatures and at temperatures below those used for synthesis
- •Catalyst can be de-waxed or contain product deposits
- •Catalyst is continuously cycled through regeneration volume containing H<sub>2</sub> and back to FT synthesis reactor volume

•H<sub>2</sub> treatment at elevated temperatures (for brief periods) be for treatment at lower temperatures led to "very high" activity

TROTAL

#### U.S. 2,479,999 Clark (1949)

Reviews known regen art and presents mechanistic basis for regen

•H<sub>2</sub> must atomically absorb on catalyst surface in order to partake in demethylation reactions with absorbed hydrocarbons

 Atomically absorbed hydrogen interacts chemically with absorbed substances and through successive demethylations, splits off methyl groups from the long chain

•Under normal synthesis (H<sub>2</sub>/CO=2) CO levels limit atomically absorbed hydrogen levels

Discloses

 Increasing temperature of operation for deactivated FT catalyst so that product consists of essentially methane

Syn gas ratio is not substantially increased

•Maintain adequate conversion level so as to allow catalyst to contact H<sub>2</sub> rich gas

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#### U.S. 2,540,109 Friedman (1951)

- Drastically reduce flow (<10 GHSV) periodically at synthesis conditions
- Temperature up to 320°C

### U.S. 2,500,056 Barr (1950)

 Continuously solvent wash catalyst using inert solvent

DITCOR

#### Overview of Cyclic Regeneration Processes

1930 - 1940

1940 – 1950

Inert gas volatilization Solvent wash H<sub>2</sub> treatment

High temperature  $H_2$  treatment Low temperature  $H_2$  treatment Oxidation  $\longrightarrow$  Reduction

Syngas treatments High H<sub>2</sub>/CO ratio Low Flow (<10 GHSV) High temperature

Low pressure

#### U.S. 2,775,607 Koelbel & Ackerman 1956

In discussing the regeneration of deactivated slurry catalyst,

"The common methods for reactivating catalyst, for example, by oxidation, hydrogenation, or extraction have little effect on these inactive catalyst suspensions. Methods which result in a substantial change of the physical or chemical condition of the catalyst are more effective"

#### **Conclusions from Early Patent** Literature

- Deactivation believed to be caused by deposits of non-desorbing products
- No quantifiable differentiation catalyst formulation
- Potential reasons for conflicting methods
  - catalyst formulations
  - time frame of measurements
  - operating conditions