The Regeneration of Hydrocarbon Synthesis Catalyst
A Partial Review of the Related Art Published during 1930 to 1952

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The published art pertaining to the Fischer Tropsch process (also known generically as Hydrocarbon Synthesis) now spans approximately 80 years. This paper addresses the patents and publications associated with catalyst regeneration as it applied to the state of the technology during the initial commercialization of the process. The review is by no means complete, however it does capture several of the key development issues and highlights the technical challenges facing companies commercializing this technology today. Although this presentation mainly focuses on patents or publications from the Great Britain and the United States, many of the patents originated in Germany at an earlier publication date.

At the end of the war, there was considerable interest in investigating and pursuing the development of the hydrocarbon synthesis process as described in Fisher’s et al publications 11, 12. A critical issue affecting the economic viability of the process involved catalyst regeneration. Commercial catalyst life was typically measured in months even under the relatively mild normal pressure synthesis conditions 11, 14, 38.

Economic analysis of the German commercial operations revealed that catalyst management cost could account for fully 1/3 of the operating staff 1. The commercial “regen” practice up through the war years was to re-work the catalyst through re-dissolving in nitric acid followed by precipitation of the catalyst components and the re-manufacturing of the catalyst. 1, 6

During the 1930’s a few publications described the treatment of aged or deactivated cobalt based catalyst with hydrogen rich treatment gas resulting in the regeneration of the lost activity 14, 35, 36. The buildup of hydrocarbon deposits over the active catalyst surface was believed to be the main cause for lost activity. Herrington and Woodward 16 presented data confirming that hydrogen was a more effective gas for regeneration as
opposed to inert materials such as nitrogen. The hydrogen appeared to react with the deposits in addition to providing a sweep gas for vaporization. In 1930 British Celanese Limited was granted a patent for regenerating deactivated hydrocarbon synthesis catalyst using hydrogen containing gas and/or steam and free of appreciable carbon monoxide or dioxide. A very similar patent (some claims are identical) was granted to Ruhrchemie in 1938. The patents claimed operations at a near synthesis conditions and at one (or higher) atmosphere pressure. Whalley was granted a patent teaching periodically stopping the flow of synthesis gas and passing an inert and non-volatile solvent through the catalyst bed as a means of “de-waxing” and thereby maintaining activity.

During the war years Roelen et al. and Sabel et al. were granted patents on improved regeneration procedures. The use of dry hydrogen gas (free of CO/CO2) successfully regenerated cobalt catalyst. Roelen et al. states that oxidation prior to reduction has been “found of advantage in the new process” but does not provide any specifics other than achieving superficial oxidation of the catalyst metal. The use of high ratio syngas (H2/CO > 2.5) at comparable temperatures as those used in hydrocarbon synthesis was found to be an effective method for regenerating any catalyst suitable for hydrocarbon synthesis. Feist was granted a patent in early 1945 teaching that high temperature hydrogen treatments were necessary for removing heavy hydrocarbon residuals from spent catalyst. Once removed these compounds would not adversely affect the subsequent dissolution with nitric acid and subsequent re-manufacturing of the commercial catalyst.

During the period immediately after the war (1945 through 1952) there were numerous patents and publications related to the re-activation steps and how to integrate these steps into the overall hydrocarbon synthesis process. Hall and Smith conducted extensive fixed bed catalyst life testing on cobalt catalysts demonstrating the effectiveness of periodic hydrogen treatments under normal pressure synthesis. The testing period under normal pressure conditions extended to approximately 400 days. Periodic treatments with high H2/CO feed gas did not restore or maintain catalyst activity.

Under medium pressure conditions the hydrogen treatment was successful during the initial operating period but became progressively less effective with catalyst age. The testing period for medium pressure operation was on the order of 150 days. The conclusion was that hydrogen treatments alone were not effective in maintaining catalyst life under normal pressure conditions. They postulated that the accumulations of relatively inactive hydrocarbon entities lead to activity loss. The medium pressure work ultimately affirmed earlier findings. The use of diluents under the medium pressure synthesis led to lower deactivation rates at the expense of total liquid yields. The use of lower gas velocities (higher conversion levels) “markedly reduces the activity of the catalyst for subsequent operations at the normal rate”. Lower ratio synthesis gas (i.e. 1.2 H2/CO) results in greater liquid yields and offered some commercial promise.

Clark reviewed the “known” regeneration methods involving solvent washing, operations at high H2/CO synthesis gas ratios, and the use of hydrogen treatments for
restoring catalyst activity. The use of elevated temperatures >270 C resulted in the regeneration of cobalt based catalyst. Clark teaches that at elevated temperatures (claiming >340 C) hydrogen can react with the deposited high boiling material responsible for the loss of activity and restore lost activity. Dreyfus \(^7\) teaches that periodically reducing pressure to sub atmospheric levels (<0.5 atm) leads to pro-longed catalyst life. Additionally the use of a diluent (up to 10X the CO level) has a similar effect. Naragon et al.\(^25\) teaches that a mild oxidation step (between 100 to 400 F with 1 to 25% O\(_2\) in N\(_2\)) will regenerate a cobalt catalyst. This patent teaches that if a slurry reactor system is utilized in the conversion process, the spent catalyst can be filtered and regenerated in the filter system or in other equipment. The use of steam at relatively high temperature (600-1000 F) followed by H\(_2\) reduction (450-750 F) also regenerated a cobalt catalyst. The preferred pressure for both of these procedures was near one atmosphere but higher pressures could be employed.

From the mid 1940’s to the early 1950’s, most patent publications (with notable exceptions) describe regeneration within the context of a fluid bed reactor system. The concept of a second catalyst for cracking and/or isomerization within a continuous fluid bed system was introduced as a method to avoid the buildup of the deactivating deposits while maintaining fluidization \(^3,8\). The interest in iron-based catalyst dominated the process patents \(^18,19,22,34\). These patents employed a separate continuous ex-situ regeneration process utilizing either a single oxidation step, combined oxidation-reduction sequence, or whatever was necessary (covering all bases). Friedman \(^13\) teaches a novel method of regenerating catalyst which has been deactivated though the deposition of carbonaceous material. In this patent, the regeneration process involves fluid bed mixing under conditions, which allow abrasion of the carbonaceous deposits from the catalyst. The unwanted material was than eluted from the bed with the effluent gas stream.

Murphee \(^24\) presents a fairly detailed disclosure of a Co based fluid bed process discussing most of the major issues associated with solids management. Similar disclosures are given by Johnson \(^21,22\). Sensel \(^30\) discloses a process configuration for a Co based fluid bed system where the regeneration step employs hydrogen at elevated temperatures to promote cracking of the hydrocarbon deposits. This process configuration introduces feed gas to both the reactor and regenerator vessels at various axial positions in order to account for the changes in gas flow due to conversion.

The post war shift from fixed bed to fluidized and slurry bed reactors led to the development of patents associated with the reduction, regeneration, and de-waxing of fine catalyst particles (2-300 microns) \(^4,23,32\). McAdams \(^23\) teaches that controlled oxidation is the method for regenerating iron catalyst and that re-reduction is not necessary. The use of a continuous solvent cleaning apparatus for finely divided solids (i.e. fluid bed or slurry reactor catalyst) is presented by Barr \(^3\).

One of the earliest disclosures of a hydrocarbon slurry reactor system was made be Stewart et. al. \(^31\). The catalyst and associated liquid is transferred from the reactor zone into a separator. The catalyst can then be filtered from the liquid and contacted with a
regenerating agent at conditions effective to restore activity. Kolbel and Ackermann discussed the ineffectiveness of the common regen methods (oxidation, reduction, extraction) on deactivated iron catalyst suspensions. They explicitly state that “Methods which result in a substantial change of the physical or chemical condition of the catalyst are more effective”. Their patent teaches a regeneration method in which the catalyst, which is carbon rich, is separated from the carbon poor fraction with the latter fraction re-introduced into the reactor.

In summary, it appears fairly obvious that there is no universal process for regenerating deactivated hydrocarbon synthesis catalysts. For the commonly studied Co and Fe catalyst system, the art over this relatively short time period contains conflicting results with patents covering a wide range of processes involving oxidation, reduction, combined oxidation-reduction, steam-reduction, operating at elevated temperatures, and several other physical methods such as solvent extraction. During this time period there was little differentiation associated with the composition of the FT catalyst (promoters, support, active surfaces). This limited literature review only encompasses a fraction of the publications over this limited time period. Further investigations will undoubtedly reveal a wider range of methods and process conditions employed in the search for a successful regeneration procedure.

Bibliography


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