

Interoffice Communication

To Charles M. Starks, Flynt Kennedy
From R. J. Convers, R. M. Owens
Date June 9, 1981
Subject Potential Plans to Handle Catalyst Life Problems at the VCM Plant

Convers by phone

*There is just DP rise in two
sill break down. Second is polymerization
of C₂H₄ & organic in pore which then
fractures pellet & breaks catalyst.
Shell indicates had some thought on polymerization
but haven't been able to find evidence of polymer
materials in cat. pellet analysis*

I. INTRODUCTION

This document is a sequel to the 5/5/81 IOC by R. J. Convers describing oxy catalyst problems at the VCM plant. The suggestions here are an outgrowth of discussions about plant operating data, lab oxy work by R. J. Convers and discussions by Exploratory Section personnel concerning the best approach for precluding the 4-5 month turnaround times which seem quite likely when O₂ based oxy and the VCM expansion become realities for Conoco (March 1983 - tentatively).

*Shell experienced
but have new
S.C.C. chg. in R-1
now (at May 1981) & balanced start-up like did in air case on this run.*

II. GENERAL APPROACH

In the absence of, or the likelihood of having, oxy pilot facilities before a plant demonstrated need, we propose a series of plant test runs in which minor catalyst changes are made in a specified fashion based on our knowledge of oxychlorination. The success of the plan hinges on plant cooperation, a general consensus that the approach is technically sound (free from catastrophic operational problems and associated economic detractors) and the ability to obtain suitably modified Harshaw catalysts. In essence success depends on our ability to sell VCM plant personnel on the idea that potential advantages would far outweigh the costs and that run times of 5-7 months (currently being experienced) would be the most disastrous thing which would happen during the sequence of tests. From preliminary considerations we speculate that additional operating costs to the plant might be in the \$100-200M range, a fairly small price to pay for extending turnaround times from 5-7 months at reduced rates (with now available catalysts) to 9-12 months at 112% of design (with a modified Harshaw system). The benefit, calculated on the basis of annualized PED turnaround cost data as a function of turnaround time could be as much as \$3.5MM for the expanded oxy operations. In the plan all experimental justification comes from historic plant operating data assuming only minor insight from our lab oxy work.

III. PROPOSED PLAN

The heart of our proposal is based on plant test runs described below. Due to time restrictions only two of the three runs could be made prior to startup of the VCM Expansion (O₂ based oxychlorination) scheduled for March 1983. This assumes ~9 month run times for each test run.

*Tumble tests of cat. & Tecosil show
no cat. breakage but show glass fines*

Run 1: A test run using the old Harshaw oxy catalyst (having porosity mainly in the 120-160 Å range) system in which the Tecosil diluent (broken glass) is replaced by a 3/16" tableted inert diluent.

*Clay material
Gives says leachability
very low in mat. per se.*

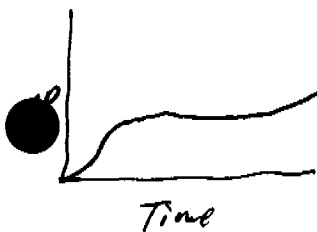
Run 2: A test run using a new Harshaw catalyst, actually a marginally modified version of the old Harshaw oxy catalyst in which the porosity is mainly in the 170-200 Å range. Again, use of this catalyst would be coupled with use of 3/16" tableted, inert diluent in place of Tecosil.

Run 3: A test run using another modified version of the catalyst used in Run 2 such that catalyst porosity is mainly in the 220-300 Å range. As before, catalyst use would be coupled with use of 3/16" tableted, inert diluent in place of Tecosil.

Logic:

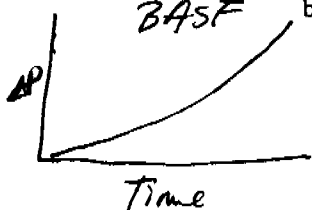
a) Historic plant run data depicts 9-10 month oxy run times at 112% of design capacity using old Harshaw catalyst (120-160 Å pore range) when run with Tecosil diluent in R-301. This is a significant improvement over current run times 5-7 mo. with SCS catalyst (at reduced capacity) or historic run times with BASF catalyst. The old Harshaw-Tecosil system exhibits high ΔP problems early in the run presumably because of poor packing properties ascribed to Tecosil in the presence of 3/16" tablets (i.e., Harshaw catalyst) - interstitial flow properties are inherently reduced using irregular shaped/sized Tecosil diluents. This system nonetheless gives 9-10 month run times because of slow coking processes with the Harshaw system.

Harshaw

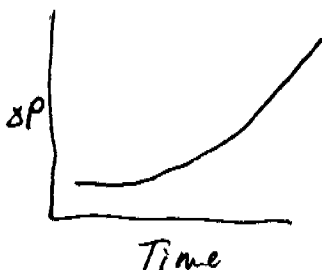


b) Historic plant data using BASF 3/16" tablets (no Tecosil) ended prematurely after ~7 mo. (at 112% of design) due to rapid coking which causes excessive ΔP problems. However, the initial stages of this run did not have high ΔP problems like those of the Harshaw-Tecosil system in a) above packed with uniformly shaped 3/16" tablets).

BASF



SCS



From a) and b), use of inert diluents shaped into 3/16" tablets in combination with Harshaw 3/16" tableted catalyst should exhibit a major operating advantage. Lower ΔP performance early in the run (10-12 psig) should extrapolate additively to longer plant run times with the Harshaw catalyst than previously experienced with the historic Harshaw-Tecosil systems. The historic Harshaw-Tecosil system characteristically operated for 9-10 months at 112% of design in air based oxy (a significant improvement over the 5-7 month runs experienced with BASF catalyst at similar rates as for the Stauffer SCS system at reduced rates). Using the old Harshaw catalyst with 3/16" tableted diluent we conservatively estimate plant run times of 11-12 months at 112% of design.

- d) BASF and Stauffer SCS catalysts (now the only catalysts available commercially) both coke up and deactivate much faster than the old Harshaw system. Present thought ascribes this condition to differences in pore size distribution of the support. BASF and Stauffer SCS catalysts have porosity distributed mainly in the 60 Å range. This contrasts the pore distribution in the old Harshaw catalyst which centers in the 120-160 Å range. Support for this position also comes from lab oxy data. Lab oxy runs using a steam calcined Catapal® alumina support (pore structure centered in the 220-250 Å range) gave short term performance data in which reduced levels of both EtCl and heavy ends (1,1,2-TCE) were observed relative to SCS or BASF systems. The latter may be particularly significant because:

- 1) heavy ends materials may inherently be formed in smaller quantities on larger pored catalysts.
- 2) once formed heavy ends materials likely escape more readily from larger pored systems than from smaller pored systems hence forming coke at diminished rates.
- 3) combined effects from 1) and 2) could be responsible for reduced coking and longer run times in a now unspecified but very dramatic fashion. The test runs suggested should help define the dependence of coking and run times on the catalyst systems in question.

The data generated from the suggested plant test runs would be inexpensive. We estimate \$100-200M of incremental plant catalyst costs. The test runs, assuming 9 month vs 6 month run times at 112% of design, more than pay for themselves. On this basis, we conservatively estimate annualized savings of \$1.2MM/yr for existing operations. In addition very timely and credible run data would be obtained for downstream use in expanded operations with even larger dividends.

IV. ALTERNATIVE POSSIBILITIES

If the plant will not accept the plan above we could develop accelerated oxy catalyst life tests in our shop. The qualities of this approach are:

- Additional time/expense in an open ended experimental approach.
- Questionable results would be obtained. Even under the best of conditions predictions of catalyst run times in the plant would be doubtful.
- Results could be obtained rapidly and cheaply.
- There would be no risk to plant operations.

All lab. tests on reaction for short time periods.

Early work said carbon ball in center of pellet that broke pellet. From Catapal O₂ burning. Converter says can't be because not enough O₂ to center of pellet. The polymerization material that breaks pellet.

Don't have right pilot p.t. for work.

Another approach would be arrange a cooperative research program with Shell to take mutual advantage of our combined resources on a mutual problem in a setting where we could take advantage of their pilot facilities.

If it were possible to arrange such a venture the data obtained would be:

- Expensive
- Highly credible (likely)
- Slow to obtain
- Risk free to plant operations

Such a program with Shell may be difficult or impossible to arrange but nonetheless contact by some process should be made with Shell to determine the extent to which they (as developers of the general O₂ based oxy technology) are concerned with, or are handling, the problems we are experiencing and foresee for the future. Contacts with Shell in this regard should probably not be made until the VCM plant's tactical position is determined.

V. TIMING

The VCM plant has been "limping along" at reduced rates with an SCS catalyst system. They will likely have a turnaround due to catalyst deactivation in mid-July. The plant plans to charge a mixed BASF-SCS system which likely will also run for only 5-6 mos. Unless we can rapidly implement our plans, the December 1981-January 1982 time frame is the earliest any of the test runs could be made at the plant. With the run times expected (9-11 mo. using Harshaw systems) one and possibly two of the suggested runs could be made prior to the March 1982 start-up for the VCM expansion. Obviously, if the plant is agreeable no time should be wasted in contacting Harshaw about preparing catalysts of interest and pursuing any necessary support functions in Exploratory Research should development of a large pore support be needed.

Implementation of beneficial results from the test runs proposed would likely not occur until after the March 1983 startup which will surely be made with Stauffer SCS catalysts to obtain contractual guarantees. Assuming an initial 4 month turnaround July 1983 would be the earliest time to implement results from the test runs proposed.

Exploratory Work Needed in Support of the Proposal

Before we approach the VCM plant with these ideas we must demonstrate that the 3/16" tableted diluent of choice does not adversely affect selectivity in the oxy system with the Harshaw catalyst in question. Such data would come from comparative oxy lab runs. In similar fashion demonstration of initial ΔP effects for the Harshaw-Tecosil vs Harshaw-tableted diluent systems would be desired.

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able. These data would come from model experiments where oxychlorination is not occurring and should help establish the credibility of our proposal to the plant.

Assuming the VCM plant is receptive to the suggested format, Harshaw must be approached concerning the preparation of the old Harshaw catalyst as well as the larger pored versions suggested. If Harshaw can prepare catalysts with the features desired we must at least screen them in the lab. If they cannot prepare them, we may have to work independently, then with them to develop the large pored support needed and test the catalysts in our lab reactor.

Apart from the catalyst support development work mentioned above we should attempt to steam calcine some preformed commercial oxy catalysts and assess the value of such an approach. This is simple, we can do it, and the technology to make the modified catalysts may be patentable.

VII. PREDICTIONS FROM PLANT AND LAB DATA

Based on plant and lab data the following predictions can be reasonably made. Again, most are extensions of demonstrated past performance.

- The catalyst concoction to be implemented by the plant in mid-July will have a 5-7 month run time. Since neither the BASF nor the SCS catalyst systems have performed well individually, there is no reason a combination should be better.
- Results from proposed Run 1 should easily mimic old Harshaw results (i.e., 9-10 month run times @ 112% of design) in the plant. Coupled with removal of the Tecosil diluent run time could be extended to 11-12 months. Even 9 month run times would be a quite favorable benefit relative to plant operations with SCS and BASF catalysts. A prediction of 11-12 month run times implies the absence of significant ΔP problems early in the run.
- Results from lab data using a steam calcined alumina support indicated the formation of significantly less ethylchloride and 1,1,2-trichloroethane than routinely seen over BASF or SCS catalysts. This trend may well be reflected in the plant setting and at least indicates no disastrous consequences from switching to a larger pored catalyst system.
- Predicting results from the larger pored catalyst runs (Runs 2 & 3) is somewhat dubious but it seems quite likely that run times in excess of 12 months could definitely be possible. Such benefits would likely occur due to diminished rates of catalyst fouling we believe would be associated with the larger pored catalysts.

Houston office says not interested in making old S.C.C. formula cat.

Not necessarily true with 32% in system

Must be willing to go with special cat. cost or back to BASF/S.C.C. No more Harshaw

If new diluent iron could be by-product increase.

VIII. PROPOSED TACTICAL SEQUENCE

- 1) Discuss recommendations and decide on best plan for handling the problems foreseen - In progress.
- 2) If plan is favorable in eyes of Chem. Res. personnel, demonstrate utility of 3/16" formed diluents in lab oxy studies and gather ΔP data as a function of gas velocity in model experiments.
- 3) If results in 2) are as predicted, discuss plan for test runs with VCM plant personnel - decide go/no go and/or modify plan so they accept if needed.
- 4) If plant agrees to plan, immediately approach Harshaw to determine feasibility for generating large pored catalysts in their shop. If yes, decide go/no go with plant and R&D input - get cost data.
- 5) If 4) is possible at Harshaw and we go, screen catalysts prepared by Harshaw to get some idea of performance expectations prior to use in the plant.
- 6) If 4) is not possible at Harshaw, provide experimental assistance from Exploratory Res. to develop large pored supports - transmit information to Harshaw and work with them to facilitate development of desired catalyst(s) - screen catalyst(s) so prepared as in 4) - coordinate preparation of commercial sized batch of catalyst at Harshaw (costs? quantities? Plant involved - R&D involved - decide go/no go with catalyst preparation) - must be done by ~6/82 (assuming Run 1 is done with a 12 month run time) to assure catalyst availability for turnaround in 1/83.
- 7) Apart from considerations 1-6, steam calcine a small sample of preformed, preloaded SCS catalyst (and perhaps others) - test catalyst(s) in lab oxy unit - decide utility of approach to large pored catalyst preparation - perhaps implement in 6 above if technically successful.

IX. POSITIVE AND NEGATIVE PLANT CONSIDERATIONS

Negatives:

- 1) Additional operating expenses to plant
 - Added cost for specially prepared catalysts
 - ~ \$100-200M
- 2) A very remote possibility that plant operations could be impaired marginally.

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Positives:

- 1) Good dividend potentially obtained for a minimum investment
 - Plant savings of ~\$3.5MM/yr seen a nominal reality for business plans based on expanded VCM operations.
 - Test runs would more than pay for themselves (~\$1.2MM/yr @ 112% design + 9 month run times).
- 2) Catalyst life data obtained - highly credible.
- 3) Worst case turnaround times would likely be 5-7 months under current operating conditions.
 - No worse than present operations.
- 4) Low market demand presently - a good time to experiment for times when optimized operations will be essential.

X. ECONOMIC SENSITIVITY TO PLANT TURNAROUND TIMES OR CATALYST LIFE

The magnitude of the economics is depicted from absolute turnaround costs assessed annually as a function of catalyst life. The values ascribed to turnaround costs were obtained from G. L. Fryar's IOC (01-11-80; Technology Evaluation Report--Shell/Stauffer Oxygen-Based Oxychlorination). Total catalyst replacement is assumed in all cases.

Catalyst Life (months)	Annualized Costs (\$MM)	Annualized Costs (\$MM)
	Existing Conoco operations (670MM lb/yr VCM)	Expanded Conoco Operations (1MMM lb/yr VCM)
4	5.42	7.33
5	4.35	5.86
6	3.63	4.88
7	3.11	4.19
8	2.72	3.66
9	2.42	3.26
10	2.18	2.93
11	1.98	2.66
12	1.81	2.44

Obviously there is a great deal in incentive to extend catalyst lifetimes to the maximum degree possible.

Robert M. Owens

Robert M. Owens
Group Leader

Ronald J. Convers

Ronald J. Convers
Senior Research Chemist

From GLF

Input from Borden is use it in heads of reactors. Not a problem. Think used as diluent in cat. when couldn't get right graded cat. because of late order. Checking to see if used in whole reactor charge & what SP looked like but not sure they know.